



DEPARTMENT OF  
**ECOLOGY**  
State of Washington

## **Quality Assurance Project Plan**

---

### **Spokane River PCBs and Other Toxics Long Term Monitoring at the Spokane Tribal Boundary**

May 2015

Publication No. 15-03-111

## Publication Information

Each study conducted by the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

This Quality Assurance Project Plan is available on Ecology's website at <https://fortress.wa.gov/ecy/publications/SummaryPages/1503111.html>

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at [www.ecy.wa.gov/eim/index.htm](http://www.ecy.wa.gov/eim/index.htm). Search Study ID BERA0012.

Ecology's Activity Tracker Code for this study is 15-047.

## Author and Contact Information

Brandee Era-Miller  
P.O. Box 47600  
Environmental Assessment Program  
Washington State Department of Ecology  
Olympia, WA 98504-7710

Communications Consultant: phone 360-407-6834.

Washington State Department of Ecology - [www.ecy.wa.gov](http://www.ecy.wa.gov)

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Yakima 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

*Any use of product or firm names in this publication is for descriptive purposes only and does not imply endorsement by the author or the Department of Ecology.*

*Accommodation Requests: To request ADA accommodation including materials in a format for the visually impaired, call Ecology at 360-407-6834. Persons with impaired hearing may call Washington Relay Service at 711. Persons with speech disability may call TTY at 877-833-6341.*

# Quality Assurance Project Plan

---

## Spokane River PCBs and Other Toxics Long Term Monitoring at the Spokane Tribal Boundary

May 2015

### Approved by:

Signature:	Date: May 2015
Adriane Borgias, Client, WQP, Eastern Regional Office	
Signature:	Date: May 2015
David T. Knight, Client's Unit Supervisor, WQP, Eastern Regional Office	
Signature:	Date: May 2015
Jim Bellatty, Client's Section Manager, WQP, Eastern Regional Office	
Signature:	Date: May 2015
Brandee Era-Miller, Author / Project Manager, EAP	
Signature:	Date: May 2015
Dale Norton, Author's Unit Supervisor, EAP	
Signature:	Date: May 2015
Will Kendra, Author's Section Manager, EAP	
Signature:	Date: May 2015
Thomas Mackie, Section Manager for Project Study Area, EAP	
Signature:	Date: May 2015
Joel Bird, Director, Manchester Environmental Laboratory	
Signature:	Date: May 2015
Bill Kammin, Ecology Quality Assurance Officer	

Signatures are not available on the Internet version.

EAP: Environmental Assessment Program

WQP: Water Quality Program

## 1.0 Table of Contents

	Page
1.0 Table of Contents .....	2
2.0 Abstract .....	6
3.0 Background .....	7
3.1 Study area and surroundings .....	7
3.1.1 Logistical problems .....	9
3.1.2 History of study area .....	9
3.1.3 Parameters of interest .....	10
3.1.4 Results of previous studies .....	10
3.1.5 Regulatory criteria or standards .....	13
4.0 Project Description .....	15
4.1 Project goals .....	16
4.2 Project objectives .....	16
4.3 Information needed and sources .....	17
4.4 Target population .....	17
4.5 Study boundaries .....	17
4.6 Tasks required .....	17
4.7 Practical constraints .....	18
4.8 Systematic planning process .....	18
5.0 Organization and Schedule .....	19
5.1 Key individuals and their responsibilities .....	19
5.2 Special training and certifications .....	20
5.3 Organization chart .....	20
5.4 Project schedule .....	20
5.5 Limitations on schedule .....	21
5.6 Budget and funding .....	21
6.0 Quality Objectives .....	24
6.1 Decision Quality Objectives (DQOs) .....	24
6.2 Measurement Quality Objectives .....	25
6.2.1 Targets for Precision, Bias, and Sensitivity .....	26
6.2.2 Targets for Comparability, Representativeness, and Completeness .....	26
7.0 Sampling Process Design (Experimental Design) .....	28
7.1 Study Design .....	28
7.1.1 Field measurements .....	29
7.1.2 Sampling location and frequency .....	29
7.1.3 Parameters to be determined .....	29
7.2 Maps or diagram .....	30
7.3 Assumptions underlying design .....	30
7.4 Relation to objectives and site characteristics .....	30
7.5 Characteristics of existing data .....	30

8.0	Sampling Procedures .....	31
8.1	Field measurement and field sampling SOPs .....	34
8.2	Containers, preservation methods, holding times .....	34
8.3	Invasive species evaluation.....	35
8.4	Equipment decontamination .....	35
8.5	Sample ID .....	36
8.6	Chain-of-custody, if required.....	36
8.7	Field log requirements .....	36
8.8	Other activities .....	36
9.0	Measurement Methods.....	37
9.1	Field procedures table/field analysis table.....	37
9.2	Lab procedures table .....	38
9.2.1	Analyte .....	39
9.2.2	Matrix .....	39
9.2.3	Number of samples.....	39
9.2.4	Expected range of results .....	39
9.2.5	Analytical method .....	39
9.2.6	Sensitivity/Method Detection Limit (MDL) .....	39
9.3	Sample preparation method(s) .....	39
9.4	Special method requirements .....	40
9.5	Lab(s) accredited for method(s).....	40
10.0	Quality Control (QC) Procedures .....	41
10.1	Table of field and lab QC required .....	41
10.2	Corrective action processes.....	42
11.0	Data Management Procedures .....	43
11.1	Data recording/reporting requirements .....	43
11.2	Laboratory data package requirements .....	43
11.3	Electronic transfer requirements .....	43
11.4	Acceptance criteria for existing data.....	43
11.5	EIM/STORET data upload procedures .....	43
12.0	Audits and Reports.....	44
12.1	Number, frequency, type, and schedule of audits .....	44
12.2	Responsible personnel .....	44
12.3	Frequency and distribution of report.....	44
12.4	Responsibility for reports.....	44
13.0	Data Verification.....	45
13.1	Field data verification, requirements, and responsibilities .....	45
13.2	Lab data verification .....	45
13.3	Validation requirements, if necessary.....	45
14.0	Data Quality (Usability) Assessment.....	46
14.1	Process for determining whether project objectives have been met .....	46
14.2	Data analysis and presentation methods .....	46
14.3	Treatment of non-detects .....	46
	Censoring for Method Blank Contamination.....	46

	Censoring for Tentatively Identified Analytes .....	47
14.4	Sampling design evaluation .....	47
14.5	Documentation of assessment.....	47
15.0	References .....	48
16.0	Figures.....	51
17.0	Tables .....	52
18.0	Appendices.....	53
	Appendix A. 303(d) Listings for Toxics in the Spokane River .....	54
	Appendix B. Continuous low-level aquatic monitoring .....	57
	Appendix C. Glossaries, Acronyms, and Abbreviations .....	60

# List of Figures and Tables

Page

## Figures

Figure 1. Spokane River Study Area. ....	8
Figure 2. Historical Average Annual Flow for the Spokane River.....	9
Figure 3. PCB Congeners in CLAM Samplers Deployed in the Spokane River.....	11
Figure 4. Total PBDEs (pg/L) in CLAM Samplers Deployed in the Spokane River.....	12
Figure 5. Concentrations of Total PCBs in Surficial Sediments. ....	13
Figure 6. Map Showing Boundary of Project Study Area. ....	15
Figure 7. CLAM Deployment Set-up. ....	32
Figure 8. Schematic of Sediment Trap Design and Deployment Configuration (Norton, 1996). ....	33

## Tables

Table 1. Parameter of Interest for the Spokane River Long-term Monitoring Station. ....	10
Table 2. Water Quality Results at the Chamokane Monitoring Site below Long Lake Dam. ....	10
Table 3. Toxics in Suspended Sediments from Sediment Traps Deployed in the Spokane River. ....	12
Table 4. Applicable Water Quality and Freshwater Sediment Standards.....	14
Table 5. Organization of Project Staff and Responsibilities.....	19
Table 6. Schedule of Field Activities for the Project.....	20
Table 7. Proposed Schedule for Completing Field and Laboratory Work, Data Entry into EIM, and Reports. ....	20
Table 8. Cost for Year 1 of Toxics Monitoring at the Spokane Tribal Border.....	21
Table 9. Budget for Surface Water Sampling in May 2015. ....	22
Table 10. Budget for Surface Water Sampling in August 2015 and January 2016. ....	23
Table 11. Budget for Analysis of Suspended Sediments.....	23
Table 12. Measurement Quality Objectives for the Study.....	25
Table 13. Surface Water Collection Methods.....	31
Table 14. Sample Containers, Preservation, and Holding Times. ....	35
Table 15. Laboratory Methods and Sample Information.....	38
Table 16. Field and Laboratory QC Samples.....	41

## 2.0 Abstract

The Spokane River is listed on the 303(d) List as impaired for water quality for PCBs and dioxins/furans. PCBs are currently being addressed through the efforts of the Spokane River Regional Toxics Task Force (SRRTTF). There is a Total Maximum Daily Load (TMDL) or Water Cleanup Plan for dissolved cadmium, lead, and zinc. There is also a fish consumption advisory for PCBs and PBDEs in the Spokane River between Idaho and Long Lake Dam.

This plan describes establishment of a long-term monitoring station for polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins/furans and metals (cadmium, copper, lead and zinc) on the mainstem Spokane River, upstream of the Spokane Tribal boundary. The planned station is downstream of all known sources of toxics and downstream of most of the current and ongoing toxics monitoring. The Spokane Tribal boundary represents an important compliance point for water quality standards, since the tribe has its own water quality standards. Monitoring toxics here over the long-term will help to indicate trends in the greater Spokane River and assess compliance with applicable water quality standards.

Ecology's Environmental Assessment Program (EAP) will establish the long-term monitoring station. Surface water and suspended sediments will be monitored annually during the 3 major hydrologic regimes for the river: spring high flow, summer low flow, and winter moderate flow.



## 3.0 Background

The Spokane River contains elevated levels of a number of toxic chemicals, including polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins/furans and metals. These contaminants are prevalent in water, sediment, and fish. Ecology first documented PCB contamination in the Spokane River in the early 1980s (Hopkins et al., 1985). Since that time, numerous studies and cleanup activities to address contamination have been conducted and are ongoing in the Spokane River watershed (Serdar et al., 2011).

The Spokane River is listed on the 303(d) List as water quality impaired for PCBs and dioxins/furans (see Appendix A for a table of all the 303(d) listings for toxics parameters in the Spokane River). PCBs are currently being addressed through the efforts of the Spokane River Regional Toxics Task Force (SRRTTF). There is a Total Maximum Daily Load (TMDL) or Water Cleanup Plan for dissolved cadmium, lead, and zinc. There are also fish consumption advisories for PCBs and PBDEs in the Spokane River between Idaho and Long Lake Dam.

Most of the current and ongoing activities to address PCBs and other toxics have focused on the upstream portion of the Spokane River, where most of the known contamination exists. For the purposes of this document, upstream Spokane River refers to areas upstream of Lake Spokane. The area downstream of Lake Spokane, below Long Lake Dam, represents an important location in the river, because it is the transition zone from waters of the state to waters of the Spokane Tribe of Indians. The Spokane Tribal boundary is where tribal water quality standards apply and their criterion for total PCBs (1.3 pg/L) is far lower than Washington's state standard for total PCBs (170 pg/L). There is currently no routine monitoring for toxic chemicals in this reach of the river to assess compliance with the state or tribal standards and evaluate trends.

With most of the known sources of toxics located upstream of Long Lake and because of its size and depth, Long Lake is probably a sink for many toxics moving downstream and depositing in lake sediments. Results from Ecology's most recent fish tissue study conducted in 2012 (Seiders et al., 2014) indicate that concentrations of PCBs and PBDEs are much lower in Little Falls Pool (the stretch of Spokane River between Long Lake Dam and Little Falls Dam) than in all the other monitoring locations upstream.

Surface water concentrations for toxics in the Spokane River below Long Lake Dam are unknown but expected to be lower than areas upstream.

## 3.1 Study area and surroundings

The Spokane River, shown in Figure 1, begins in Idaho at the outlet of Lake Coeur d'Alene and flows west 112 miles to the Columbia River. The Spokane River watershed encompasses over 6,000 square miles in Washington and Idaho (Serdar et al., 2011). The river flows through the smaller cities of Post Falls and Coeur d'Alene in Idaho and large urban and industrial areas in Spokane Valley and Spokane in Washington. Other cities include Liberty Lake in Washington as well as Wallace and Kellogg in Idaho, upstream of Lake Coeur d'Alene. The Spokane Tribe

of Indians reservation encompasses the north bank of the lower river from Chamokane Creek, below Long Lake Dam, downstream to the Columbia River.

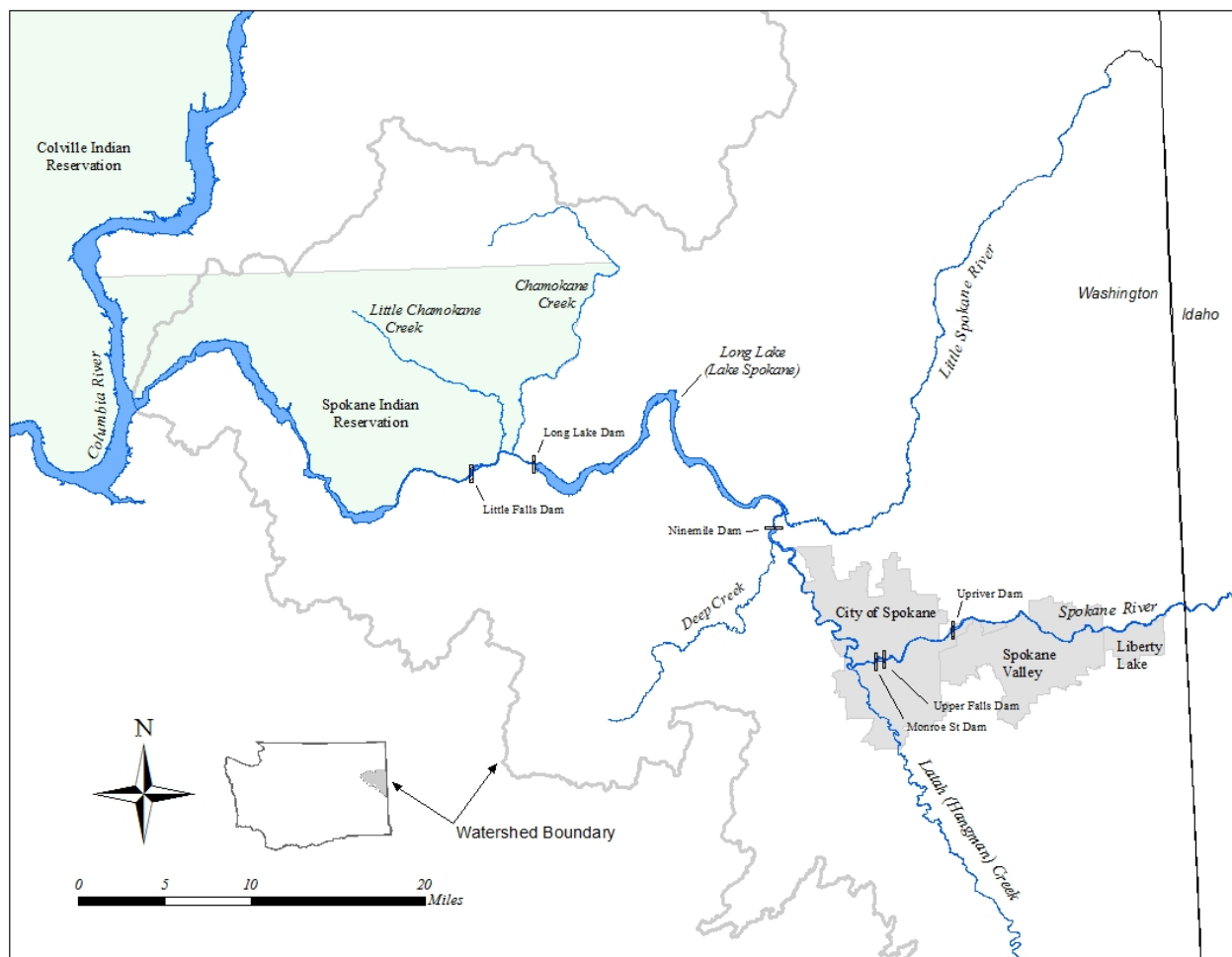


Figure 1. Spokane River Study Area.

The Spokane River sits atop the western portion of the Spokane Valley-Rathdrum Prairie Aquifer. There is significant interchange between the river and the aquifer. The river is the largest contributor to the aquifer (49% of aquifer inflow) but is also the largest recipient of aquifer water, at about 58% of river outflow (MacInnis et al., 2009).

The Spokane River is impacted by 7 major dams that create reservoirs behind them. From upstream to downstream they are: Post Falls Dam, Upriver Dam, Upper Falls Dam, Monroe Street Dam, Nine Mile Dam, Long Lake Dam and Little Falls Dam.

The Spokane River watershed is located in a transition area between the barren scablands of the Columbia Basin to the west, coniferous forests and mountainous regions to the north and east, and prairie lands to the south. Spokane receives 16.5 inches of rain annually on average. Spring snowmelt dominates flows in the Spokane River from April through June as shown in Figure 2.

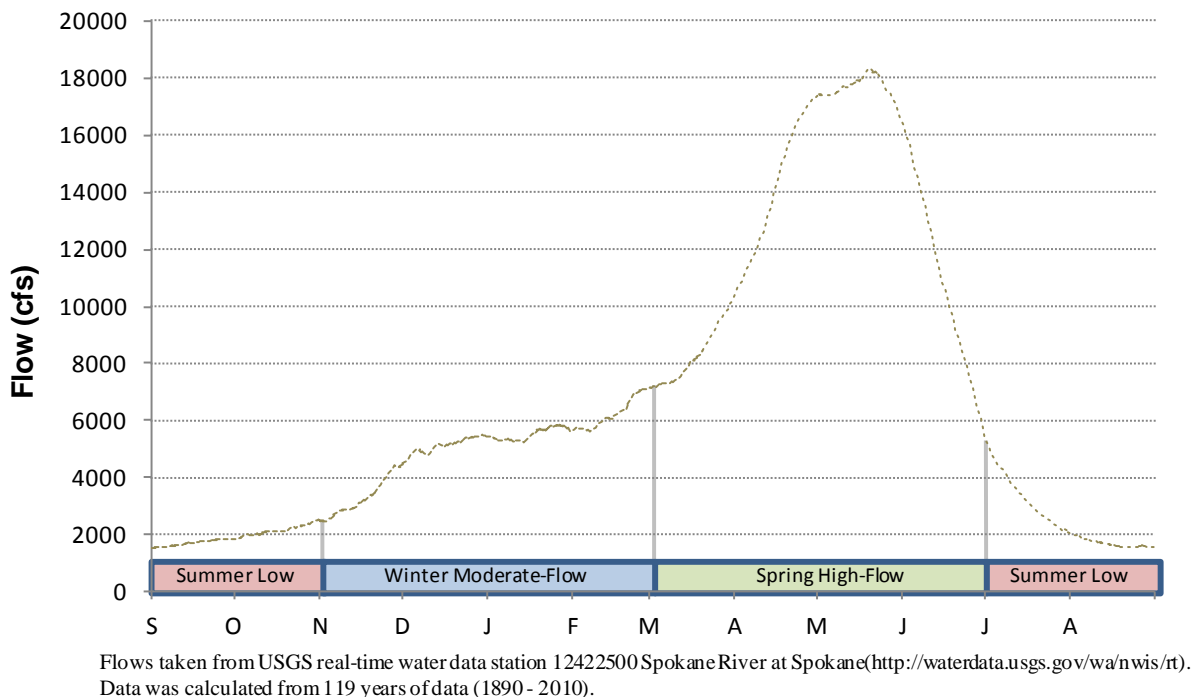


Figure 2. Historical Average Annual Flow for the Spokane River.

### 3.1.1 Logistical problems

Water depths and currents in the Spokane River below Long Lake Dam present potential logistical problems for the project. At least 10 feet of depth is required to deploy sediment traps so that they sit safely below the water's surface. The depth of the water at the pool area downstream of the highway 231 (known locally as Spring Creek Road) bridge is estimated to be much deeper than 10 feet. Strong currents can also make retrieval of sediment traps difficult.

Ecology has permission to sample surface water at the two potential monitoring locations for the study: Avista Park (on the south bank just below Long Lake Dam) and at the Union Gospel Mission (on the north bank just upstream of Chamokane Creek). The planned surface water sampling will take up to 36 hours. As long as water levels don't fluctuate more than a few inches during the <36 hour sampling period, sampling should not be affected. With reconnaissance of both locations, we can choose the site that will work best for surface water sampling. Depth of water will be a determining factor. Depths of least 2 feet will make deployment of CLAMs (Continuous Low-level Aqueous Monitoring device) possible.

### 3.1.2 History of study area

As stated in the *Background* section of this QA Project Plan, Ecology first documented PCB contamination in the Spokane River in the early 1980s (Hopkins et al., 1985). Since that time, Ecology has conducted numerous on-going studies and cleanup activities to address contamination in the Spokane River watershed (Serdar et al., 2011).

The Spokane River is a valuable resource to all watershed inhabitants, including the people who live there. The Spokane Valley – Rathdrum Prairie Aquifer, which interchanges substantially with the river, provides drinking water to more than 500,000 people (MacInnis et al., 2009). Many people use the river for fishing, swimming, and boating. Numerous dams provide electricity and flood control.

The Spokane Tribe of Indians’ reservation borders the lower section of the river from Chamokane Creek down to the Columbia River (Figure 1). This river has been an important source of food and ceremony for the Spokane Tribe for centuries.

### 3.1.3 Parameters of interest

Parameters of interest for the project are presented in Table 1.

Table 1. Parameter of Interest for the Spokane River Long-term Monitoring Station.

Parameter	Reason for Interest in Spokane River
PCBs	303(d) listed, fish consumption advisory <sup>1</sup> , focus of Spokane River Regional Toxics Task Force (SRRTTF).
PBDEs	Fish consumption advisory <sup>1</sup>
Dioxin/furans	303(d) listed
Cadmium, Lead and Zinc	A TMDL <sup>2</sup> for dissolved metals has been implemented

<sup>1</sup> DOH, 2009.

<sup>2</sup> Butkus and Merrill, 1999.

### 3.1.4 Results of previous studies

Numerous data sets exist for toxics in the Spokane River (too many to list here). A few select studies including data from Ecology’s 2012-2013 toxics sampling (Era-Miller, 2014) are discussed in this section.

Table 2 indicates the total and dissolved organic carbon content (TOC and DOC) and total suspended solids (TSS) in surface water near the proposed monitoring site. Concentrations of these parameters are generally quite low and are usually measured near analytical reporting limits.

Table 2. Water Quality Results at the Chamokane Monitoring Site below Long Lake Dam.

Parameter	Result (mg/L)	
	10/24/12 – 10/25/12	5/23/13 – 5/24/13
DOC	1 U	1.1
TOC	1 U	1.2
TSS	1 U	2

U: the analyte was not detected at or above the reported result.

Data from Era-Miller, 2014.

The Spokane Tribe records continuous dissolved oxygen, temperature, and conductivity with a hydrolab from June through October at the Union Gospel Mission (UGM) site located on the north bank of the river just upstream of Chamokane Creek (Brian Crossley, personal communication).

Ecology's Statewide River and Stream Ambient Monitoring Program has a station (54A070) located at the Highway 231 bridge (also known locally as Spring Creek Bridge). Relevant data collected here includes DOC, TOC, TSS, turbidity, conductivity, temperature, hardness, and flow. A search in Ecology's EIM database shows that data for some of these parameters span from 1959 through 2010.

Figure 3 shows total PCB congener results for CLAMs (Continuous Low-level Aqueous Monitoring device) deployed by Ecology at Upriver Dam and Nine Mile Dam in fall of 2012 compared to the water quality standards applicable to the Spokane River. The Day 2 results give an indication of the dissolved fraction of PCBs where CLAMs with and without prefilters (1.5 micron size) were compared. Figure 4 gives the results for PBDE congeners in CLAMs from the same deployments (Era-Miller, 2014)

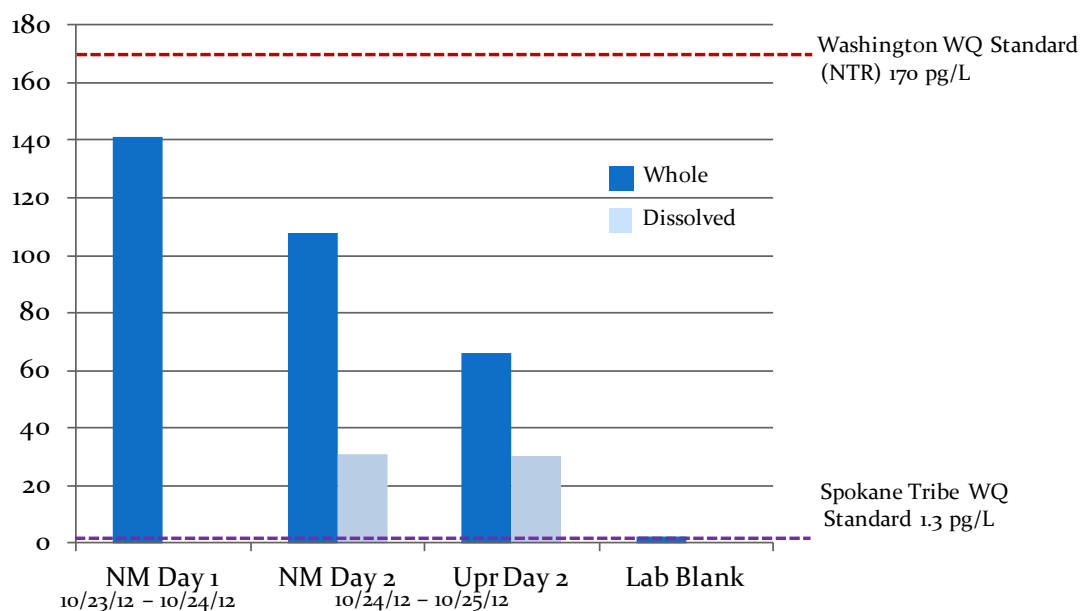


Figure 3. PCB Congeners in CLAM Samplers Deployed in the Spokane River.

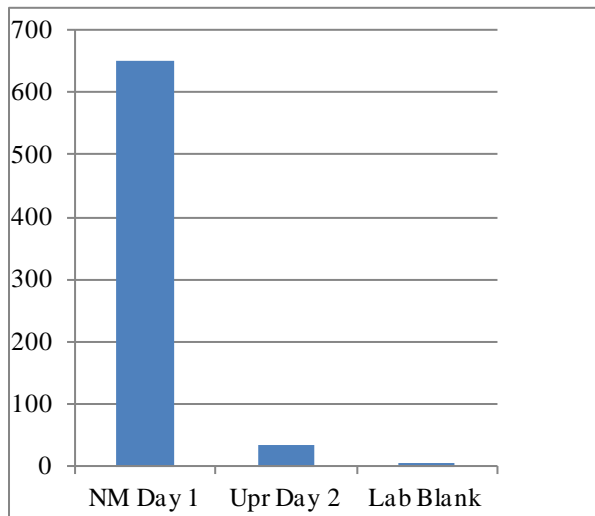


Figure 4. Total PBDEs (pg/L) in CLAM Samplers Deployed in the Spokane River.

Table 3. Shows PCB, PBDE, metals, and dioxin TEQ (toxic equivalency) results for suspended sediments near Ninemile Dam and Upriver Dam where the CLAM data was collected in 2012 (Era-Miller, 2014).

Table 3. Toxics in Suspended Sediments from Sediment Traps Deployed in the Spokane River.

Location Dates Deployment Period Sample No.	Ninemile Dam			Upriver Dam		Lab Method Blank
	10/10/12 - 2/1/13		2/1/13 - 6/13/13	10/9/12 -1/31/13	1/31/13 - 4/9/13	
	113 days		132 days	113 days	68 days	
	1304017-01	Replicate	1306061-01	1304017-02	1304017-03	
% Solids	42.9	42.8	33.5	18.3	19.5	ND
% TOC	3.9	3.8	7.4	11.0	12.9	ND
<i>Metals (mg/Kg, dry weight) ppm</i>						
Cadmium	5	5	8	22	24	ND
Lead	85	83	213	825	640	ND
Zinc	822	777	1130	2,580	2,420	ND
<i>Organics (dry weight)</i>						
Total PCBs (ug/Kg) ppb	13.7 J	13.8 J	17.2	28.5 J	25.4 J	0.13 J
Total PBDEs (ug/Kg) ppb	65.2	58.2	23.6	22.5	19.2	0.04
Dioxin TEQ (ng/Kg) pptr	1.6	0.7	0.6	1.3	4.5	0.0

ND: not detected

J: result value in an estimate

TEQ: toxic equivalency

Perhaps the best indicator of what the concentrations of PCBs in suspended sediments from the proposed monitoring site will be, relative to other locations in the Spokane River, is data from the 2003-2007 Spokane River Source Assessment (Serdar et al., 2011). Figure 5 indicates that surficial sediments (top 2 cm) from behind Little Falls Dam are comparatively lower in PCBs. Results in Figure 5 are normalized to organic carbon. Buffalo Lake was used as a reference site for the source assessment and is shown in Figure 5.

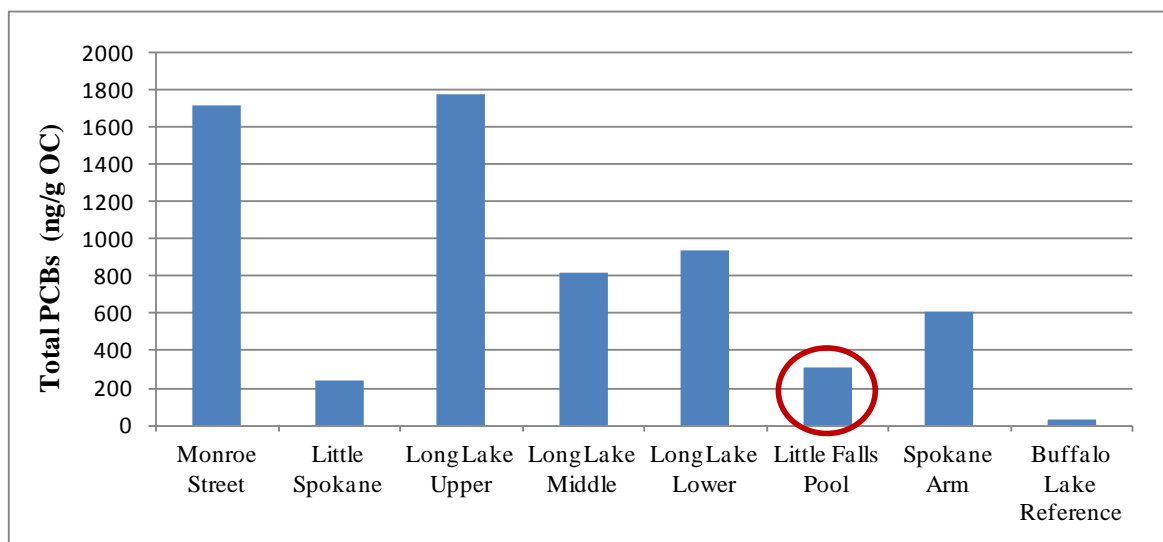


Figure 5. Concentrations of Total PCBs in Surficial Sediments.

Ecology's 2012 comprehensive fish tissue study is another source of data that indirectly relates to—but may also be a good indicator for—toxics levels in the Spokane River downstream of Long Lake Dam is (Seiders et al., 2014). Largescale suckers from Little Falls Pool (the river between Long Lake Dam and Little Falls Dam) were analyzed for PCBs and PBDEs. Concentrations in these fish were lower than concentrations in fish at the 5 other sampling locations, which were all upstream, including the state line with Idaho.

### 3.1.5 Regulatory criteria or standards

The main objective for this study is to generate seasonal monitoring data (based on the 3 major flow periods: spring high-flow, summer low-flow and winter moderate-flow) that can be used to indicate significant ( $p < 0.05$ ) trends for toxics in the Spokane River over time. Data may be compared to the standards in Table 4.

Table 4. Applicable Water Quality and Freshwater Sediment Standards.

Parameter	Matrix	WA State Standards <sup>a,b</sup>	Spokane Tribal Standards <sup>c</sup>
Total PCBs	Surface Water	170 pg/L	1.3 pg/L
PBDEs		NA	NA
Copper		Hardness dependant	Hardness dependant
Cadmium			
Lead			
Zinc			
Total PCBs <sup>1</sup>	Sediments	110 ug/Kg dw	NA
PBDEs		NA	
Dioxins/furans		NA	
Copper		400 mg/Kg dw	
Cadmium		2.1 mg/Kg dw	
Lead		360 mg/Kg dw	
Zinc		3200 mg/Kg dw	

NA: Not applicable

<sup>a</sup> WAC 173-201A

<sup>b</sup> WAC 173-204

<sup>c</sup> Spokane Tribe of Indians, 2010

<sup>1</sup> Based on total Aroclors



## 4.0 Project Description

Ecology will establish a long-term monitoring station for PCBs, PBDEs, dioxins/furans, and metals (cadmium, copper, lead and zinc) at the upper Spokane Tribal boundary on the lower portion of the Spokane River. The Spokane River is listed as water quality-impaired for PCBs and dioxins/furans. PCBs are currently being addressed through the efforts of the Spokane River Regional Toxics Task Force (SRRTTF). There is a Total Maximum Daily Load (TMDL) or Water Cleanup Plan for cadmium, lead, and zinc. There is also a fish consumption advisory for PCBs and PBDEs in the Spokane River between Idaho and Long Lake Dam.

The planned long-term monitoring location (Figure 6) is downstream of all known sources of toxics and downstream of most of the current and ongoing toxics monitoring. The Spokane Tribal boundary represents an important compliance point for water quality standards, since there is a transition from the Washington state standards (WAC 173-201A) to the tribal standards (Spokane Tribe of Indians, 2010). Monitoring toxics here over the long-term will help us evaluate compliance with applicable water quality standards and trends over time in the Spokane River.

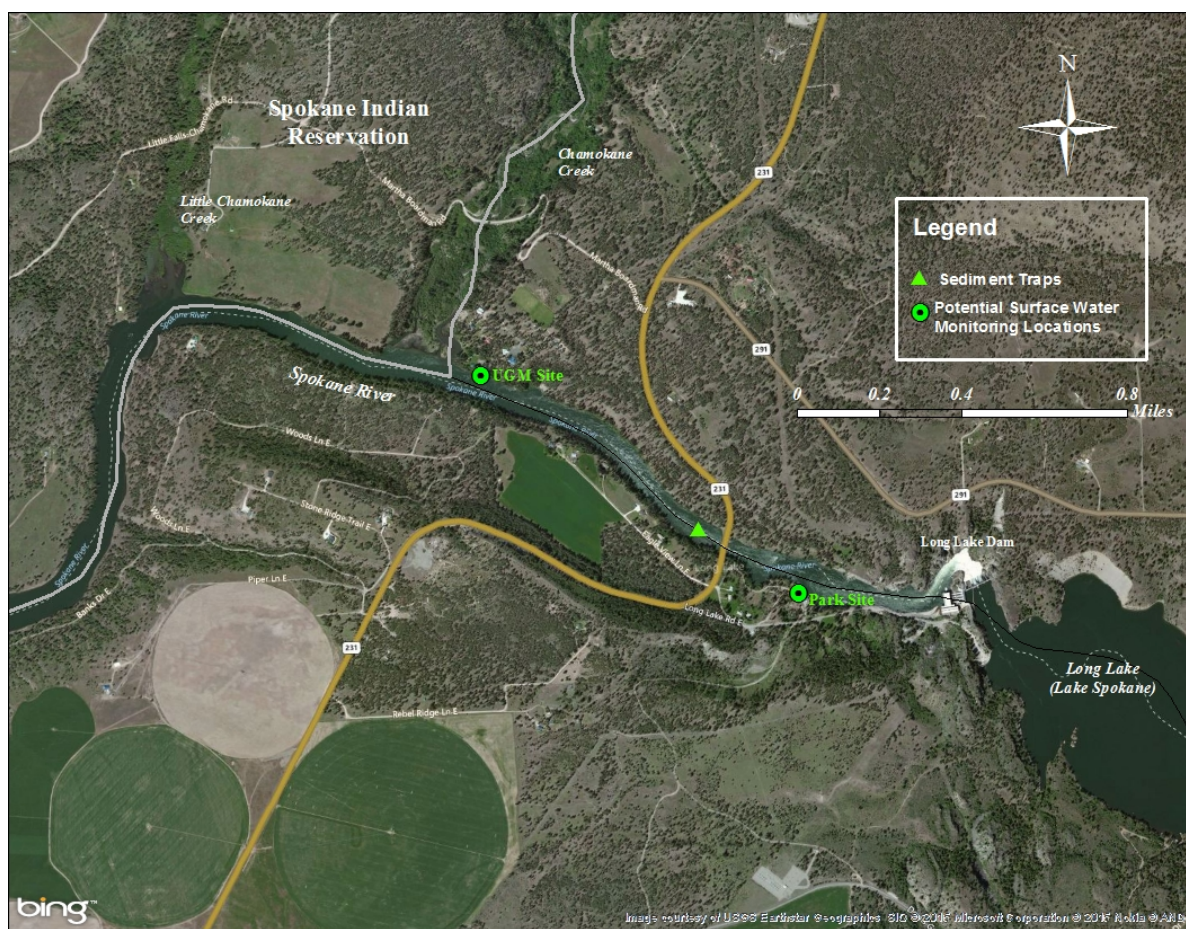


Figure 6. Map Showing Boundary of Project Study Area.

Ecology's Environmental Assessment Program (EAP) will establish the long-term monitoring station. Surface water and suspended sediments will be monitored annually during the 3 major hydrologic regimes in the river: spring high flow, summer low flow, and winter moderate flow.

The Spokane River long-term station will be included in a larger effort by EAP to assess the efficacy of various types of high volume techniques for collecting low-level organics in surface water. The QA Project Plan for the high volume study is currently in development. Because the Spokane River long-term station will be included in this larger effort, both CLAM and 20-liter composite samples will be analyzed for PCBs and PBDEs for the first year of monitoring. In addition, a high number of field replicates and laboratory quality control samples will be taken during the first year of monitoring.

Specifics for a high-volume validation study for low-level organics and an SOP (standard operating procedure) for the use of CLAMs will be laid out in a QA Project Plan to be authored by EAP in mid 2015.

## 4.1 Project goals

Goals for the project are to:

- Establish a long-term monitoring station for toxics at the Spokane Tribal Boundary. Data from the first year of monitoring at the long-term station will be used to design a long-term trend program for the site. Such a long-term monitoring program would likely be in place for more than 10 years, because PCBs are persistent chemicals. To reduce their presence in the river to meet water quality standards will likely take decades.
- Characterize toxics in surface water and suspended sediments at the monitoring station during 3 hydrologic regimes for the river: spring high flow, summer low flow and winter moderate flow.
- Use data from the study to support the development of standard operating procedures (SOP) for use of the CLAM collection device and the proposed validation study for various high-volume surface water collection techniques for low-level organics. The goal of the proposed high-volume study is to characterize the precision and accuracy of different high-volume collection methods for use with low-level analytical methods like the EPA 1600 series methods, with special focus on PCBs.

## 4.2 Project objectives

Objectives for the project are to:

- Collect and characterize surface water samples for select toxics during 3 hydrologic regimes for the Spokane River: spring high flow, summer low flow and winter moderate flow at the Spokane Tribal boundary station to evaluate seasonal variability in concentrations of target parameters.

- Collect and characterize suspended sediments for select toxics on an annual basis by having sediment traps deployed continuously for one year. Traps will be set to collect for 4 months at a time with 3 deployments each year.
- Provide high quality data to support the development of standard operating procedures (SOP) for use of the CLAM collection device and the proposed validation study for high-volume surface water collection techniques.

### 4.3 Information needed and sources

River flow data from Avista Utilities, owner and operator of Long Lake Dam, will be needed to calculate flux for sediment traps and useful to calculate loads for surface water toxics.

### 4.4 Target population

Parameter	Surface Water	Suspended Sediment
PCB congeners	X	X
PBDEs	X	X
Dioxin/furans		X
Metals <sup>†</sup>	X	X

<sup>†</sup> Cadmium, copper, lead and zinc

### 4.5 Study boundaries

The study will characterize surface water conditions for select toxics in the lower Spokane River downstream of Long Lake Dam and upstream of the Spokane Tribal boundary and upstream of Chamokane Creek. See Figure 1 for extent of the Spokane River Watershed boundary within Washington and Figure 6 for the proposed monitoring locations for the study.

The Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area are:

- WRIA 54
- HUC number 17010307

### 4.6 Tasks required

- Reconnaissance of the sampling area in late March or early April 2015 to decide whether the Park site or the UGM site will be better for surface water collection.
- Submit a bid solicitation by mid March 2015 for the toxics analyses to be conducted by contract laboratory.

- Work in tandem with other Ecology studies, including the proposed validation study for high-volume collection methods to maximize efficiencies with quality assurance/quality control (QA/QC) samples and purchasing of equipment.
- Purchase and acquire equipment needed for surface water and suspended sediment monitoring.
- Prepare all materials needed for sampling (e.g., special cleaning for low-level toxics, bottles, labels, and paperwork).

## **4.7 Practical constraints**

Practical constraints for this project mostly revolve around high-flow/low-flow sampling issues for both surface water and suspended sediments. Reconnaissance of the sampling area in late March or early April 2015 and obtaining flow information from Long Lake Dam through Avista Utilities should help to better inform sampling and avoid potential problems.

## **4.8 Systematic planning process**

Not Applicable.

## 5.0 Organization and Schedule

### 5.1 Key individuals and their responsibilities

Table 5. Organization of Project Staff and Responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Adriane Borgias Water Quality Program Eastern Regional Office Phone: 509-329-3515	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Brandee Era-Miller Toxics Studies Unit, SCS Phone: 360-407-6771	Project Manager/Principal Investigator	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
William Hobbs Toxics Studies Unit, SCS Phone: 360-407-7512	Field and Project Assistant – QAPP Peer Review	Reviews QAPP. Provides input on project use of high-volume sample collection for low-level organics. Helps collect samples and records field information.
Melissa McCall Toxics Studies Unit, SCS Phone: 360-407-7384	Field Assistant	Helps collect samples and records field information.
Dale Norton Toxics Studies Unit, SCS Phone: 360-407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra SCS Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Thomas Mackie Eastern Operations Section Phone: 509-457-7136	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Joel Bird Manchester Environmental Laboratory Phone: 360-871-8801	Director	Reviews and approves the final QAPP.
Contract Laboratory	Project Manager	Reviews draft QAPP, coordinates with MEL QA Coordinator
Karin Feddersen Phone: 360-871-8829	MEL QA Coordinator	Helps project manager work with contract laboratory for contracting and conducts a QA review of data packages from the contract laboratory.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

QAPP: Quality Assurance Project Plan

SCS: Statewide Coordination Section



## 5.2 Special training and certifications

The project lead, Brandee Era-Miller, has almost 15 years of experience conducting toxics studies and writing reports for Ecology's EAP Toxics Studies Unit.

## 5.3 Organization chart

Not Applicable.

## 5.4 Project schedule

A schedule of fieldwork for the project is shown in Table 6. The first surface water sampling (using both CLAM collection device and 20-liter composite samples) will occur in early May 2015 and again in August 2015 and January 2016. Sediment traps will be deployed continuously for collection of suspended sediments for a year. Traps will be retrieved, sampled, and collection cylinders re-placed every 4 months. The first deployment is slated for April 2015. The long-term plan is for sampling on this schedule annually.

Table 6. Schedule of Field Activities for the Project.

Field Activity	Apr-15	May-15	Jun-15	Jul-15	Aug-15	Sep-15	Oct-15	Nov-15	Dec-15	Jan-16	Feb-16	Mar-16
CLAM and 20 L sampling		*			*					*		
Sediment Trap Deployments	Spring High Flow				Summer Low Flow				Winter Moderate Flow			

\*surface water sampling will occur over a 24-36 hour period

Table 7. Proposed Schedule for Completing Field and Laboratory Work, Data Entry into EIM, and Reports.

Field and laboratory work	Due date	Lead staff
Field work completed	March 2016	Brandee Era-Miller
Laboratory analyses completed	June 2016	
Environmental Information System (EIM) database		
EIM Study ID	BERA0012	
Product	Due date	Lead staff
EIM data loaded	September 2016	Brandee Era-Miller
EIM data entry review	October 2016	Melissa McCall
EIM complete	November 2016	Brandee Era-Miller
Final report		
Author lead / Support staff	Brandee Era-Miller	
Schedule		
Draft due to supervisor	August 2016	
Draft due to client/peer reviewer	September 2016	
Draft due to external reviewer(s)	October 2016	
Final (all reviews done) due to publications coordinator	November 2016	
Final report due on web	December 2016	

## 5.5 Limitations on schedule

Reserving sample collection equipment such as a Hydrolab, CLAM devices, sediment traps and a boat (for sediment trap deployment) will need to be considered for scheduling. Availability of field staff to assist in fieldwork will also need to be considered.

All EAP staff, including the project manager, are current on their first Aid/CPR, defensive driving and EAP-specific safety training. The following sections from EAP's Safety Manual (EAP, 2014) are relevant to this project and will be reviewed by staff prior to conducting fieldwork:

- Chemical Use in EAP Specialized Rooms
- Working in Rivers and Streams
- Winter Safety/Hypothermia
- Preventing Heat-Related Injuries
- Towing Trailers
- EAP Boating Plan
- Operating 16' Wooldridge Jet Boat

## 5.6 Budget and funding

The cost for the first year of toxics monitoring in the Spokane River at the Spokane Tribal Border is **\$74,563** (Table 8). The budget is further detailed in Tables 9 and 10.

Table 8. Cost for Year 1 of Toxics Monitoring at the Spokane Tribal Border.

\$	27,890	May 2015 Surface Water Sampling
\$	31,440	August 2015 and January 2016 Surface Water Sampling
\$	15,234	Annual (3 deployments) Suspended Sediment Sampling
\$	<b>74,563</b>	<b>Total Project Cost for Year 1 Monitoring</b>

Surface water sampling conducted in May 2015 will be funded from fiscal year 2015 (FY15) budget, as shown in Table 9. The rest of the project work will be funded from fiscal year 2016 budget, which starts July 1, 2015 (Tables 10 and 11).

Table 9. Budget for Surface Water Sampling in May 2015.

Parameters	Numbers of Samples	Number of QA Samples	Total Numbers of Samples	Cost Per Sample	MEL Subtotal	Contract Lab Subtotal
<i>Surface Water (20 liters)</i>						
PCB Congeners (1668c)	2	2	4	888	--	3552
PBDEs (1614)	2	2	4	888	--	3552
20 liter canister proofing	NA	1	1	1200	--	1200
DOC	1	1	2	45	90	--
TOC	1	1	2	45	90	--
TNVSS	1	1	2	27	54	--
Hardness	2	2	4	23	92	--
Cd, Cu, Pb and Zn (low-level)	4	3	7	132	924	--
Metals bottle, filters and acid	4	3	7	60	420	--
Shipping Costs	1	4	5	50	--	250
<i>Surface Water (CLAM)</i>						
PCB Congeners (HR)	5	1	6	700	--	4200
PBDEs (1614)	5	1	6	700	--	4200
SPE Method Blank	NA	1	1	1300	--	1300
SPE OPR	NA	1	1	1300	--	1300
SPE Disk Conditioning	5	2	7	50	--	350
Field spiking	3	2	5	25	--	125
SPE Disks*	7	7	14	89	--	1246
Totalizers	3	0	3	0	--	0
*used for CLAM and 20 liter samples			MEL Lab subtotal		\$ 1,670	
			Contract Lab subtotal		\$ 21,275	
			Contract Fee (25 %)		\$ 4,945	
			Grand Total		<b>\$ 27,890</b>	

The budget for surface water samples collected in August 2015 and January 2016 is shown in Table 10. The items highlighted in yellow will be funded by the Spokane River Long-Term Monitoring Station project and the gray highlighted items will be funded by the high volume validation study for low-level organics (QA Project Plan in draft).

Table 11 gives the annual (3 deployments of 4 months each) budget for analysis of the suspended sediment samples collected with sediment traps.



Table 10. Budget for Surface Water Sampling in August 2015 and January 2016.

Parameters	Numbers of Samples	Number of QA Samples	Total Numbers of Samples	Cost Per Sample	MEL Subtotal	Contract Lab Subtotal
<b>Surface Water (20 liters)</b>						
PCB Congeners (1668c)	4	4	8	888	--	7104
PBDEs (1614)	4	4	8	888	--	7104
20 liter canister proofing	NA	1	1	1200		1200
DOC	2	2	4	45	180	--
TOC	2	2	4	45	180	--
TNVSS	2	2	4	27	108	--
Hardness	4	4	8	23	184	--
Cd, Cu, Pb and Zn (low-level)	8	6	14	132	1848	--
Metals bottle, filters and acid	8	6	14	60	840	--
Shipping Costs	2	8	10	50	--	500
<b>Surface Water (CLAM)</b>						
PCB Congeners (HR)	10	2	12	700	--	8400
PBDEs (1614)	10	2	12	700	--	8400
SPE Method Blank	NA	2	2	1300	--	2600
SPE OPR	NA	2	2	1300	--	2600
SPE Disk Conditioning	10	4	14	50	--	700
Field spiking	6	4	10	25	--	250
SPE Disks*	14	14	28	89	--	2492
Totalizers	6	0	6	0	--	0
*used for CLAM and 20 liter samples			MEL Lab subtotal		\$ 2,872	
Project costs in yellow highlight and italics			Contract Lab subtotal		\$ 22,854	
			Contract Fee (25 %)		\$ 5,714	
			Grand Total		\$ 31,440	

Table 11. Budget for Analysis of Suspended Sediments.

Parameters	Numbers of Samples	Number of QA Samples	Total Numbers of Samples	Cost Per Sample	MEL Subtotal	Contract Lab Subtotal
PCB Congeners (1668c)	3	3	6	700	--	4200
PBDEs (1614)	3	3	6	650	--	3900
Dioxins/furans (1613b)	3	3	6	550	--	3300
Metals -Cd, Cu, Pb & Zn	3	3	6	107	642	--
Percent Solids	3	3	6	12	72	--
TOC	3	3	6	45	270	--
			MEL Lab subtotal		\$ 984	
			Contract Lab subtotal		\$ 11,400	
			Contract Fee (25 %)		\$ 2,850	
			Grand Total		\$ 15,234	

## **6.0 Quality Objectives**

### **6.1 Decision Quality Objectives (DQOs)**

One quality objective for this project is to obtain data of sufficient quality to minimize uncertainty. For monitoring using continuous low-level aquatic monitoring (CLAM) samplers and 20 liter surface water samples, the objective is to produce enough field duplicate data and laboratory quality assurance and quality control (QA/QC) data to assist in evaluating the precision and accuracy of these collection methods and analytical methods. This will be a major objective of the proposed high-volume validation study for which the first year of monitoring data from the Spokane Tribal boundary site will be included. Precision and accuracy information will be used to inform the development of a long-term monitoring program to evaluate trends in select toxics at the Spokane Tribal boundary site.

Ecology's Manchester Environmental Laboratory (MEL) and laboratories contracted by MEL for analysis of project samples are expected to meet the measurement quality objectives (MQOs) selected for the project. The MQOs that will be used for the project are shown in Table 12.

## 6.2 Measurement Quality Objectives

Table 12. Measurement Quality Objectives for the Study.

Parameter	Analytical Method	Lab Control Samples (% Recovery)	Duplicate Samples (RPD)	Matrix Spike (% Recovery)	Matrix Spike Duplicates (RPD)	Surrogate Recoveries (% Recovery)
<b>Surface Water (20 Liter, 1 gallon and grabs)</b>						
TOC & DOC	SM 5310B	80 – 120	≤20%	75 – 125	≤20%	NA
TSS	SM 2540D	80 – 120	≤20%	NA	NA	NA
TNVSS	SM 2540B/E	80 – 120	≤20%	NA	NA	NA
Hardness*	SM 2340B	85 – 115	≤20%	75 – 125	≤20%	NA
Cd, Cu, Pb, & Zn*	EPA 200.8	85 – 115	≤20%	75 – 125	≤20%	NA
PCBs	EPA 1668c	50 – 150 <sup>†</sup>	≤50%	NA	NA	25 – 150 <sup>a</sup>
PBDEs	EPA 1614	50 – 150 <sup>†</sup>	≤50%	NA	NA	25 – 150 <sup>a,b</sup>
<b>Surface Water (CLAM)</b>						
PCBs	EPA 1668c	50 – 150 <sup>†</sup>	≤50%	NA	NA	25 – 150 <sup>a</sup>
PBDEs	EPA 1614	50 – 150 <sup>†</sup>	≤50%	NA	NA	25 – 150 <sup>a,b</sup>
<b>Suspended Sediments</b>						
% Solids	SM 2540G	NA	≤20%	NA	NA	NA
TOC	PSEP – TOC	80 – 120	≤20%	NA	NA	NA
Cd, Cu, Pb, & Zn	EPA 200.7	85 – 115	≤20%	75 – 125	≤20%	NA
PCBs	EPA 1668c	50 – 150 <sup>†</sup>	≤50%	NA	NA	25 – 150 <sup>a</sup>
PBDEs	EPA 1614	50 – 150 <sup>†</sup>	≤50%	NA	NA	25 – 150 <sup>a,b</sup>
Dioxins/furans	EPA 1613	25 – 150 <sup>†</sup>	≤50%	NA	NA	25 – 150 <sup>a</sup>

\* hardness and metals collected as single grab samples

<sup>†</sup> Per Method for Ongoing Precision and Recovery (OPR), internal standards, and labeled compounds

<sup>a</sup> labeled congeners

<sup>b</sup> PBDE 209 recovery of 20 – 200%

CLAM: Continuous Low-Level Aquatic Monitoring device

EPA: the Environmental Protection Agency

SM: Standard Methods

PSEP: Puget Sound Estuary Protocols

RPD: relative percent difference

TOC: total organic carbon

TSS: total suspended solids

TNVSS: total non-volatile suspended solids

DOC: dissolved organic carbon

Cd: cadmium; Cu: copper; Pb: lead; and Zn: zinc

## 6.2.1 Targets for Precision, Bias, and Sensitivity

### 6.2.1.1 Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Precision for two replicate samples is measured as the relative percent difference (RPD) between the two results. If there are more than two replicate samples then precision is measured as the relative standard deviation (RSD).

Measurement quality objectives for the precision of laboratory duplicate samples and matrix spike duplicate samples are shown in Table 12. PCBs and PBDEs in both the 20-liter and CLAM surface water samples will be analyzed as field triplicates during the May 2015 sampling. Acceptance limits for field precision of these samples is  $\leq 20$  RSD. CLAMs deployed in triplicate in the Spokane River in 2012 were 11% and 14% for total PCBs and 9% and 19% for total PBDEs (Era-Miller, 2014).

### 6.2.1.2 Bias

Bias is the difference between the population mean and the true value. For this project, bias is measured as acceptable % recovery. Acceptance limits for laboratory control samples (LCS), matrix spikes and surrogates are shown in Table 12. Calibration of field instruments will also reduce the bias of field measurements.

### 6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance above the background noise of the analytical system. The laboratory reporting limits (RLs) for the project are described in Section 9.2.

## 6.2.2 Targets for Comparability, Representativeness, and Completeness

### 6.2.2.1 Comparability

Section 8.1 lists the standardized operating procedures (SOPs) to be followed for field sampling. Appendix B gives a summary of the field and laboratory procedures used by EAP for sample collection using CLAMs. All analytical methods used for the project are approved methods commonly used by Ecology and other entities in the Spokane River watershed for monitoring of toxics.

### 6.2.2.2 Representativeness

Surface water and suspended sediment samples will be collected during the 3 major flow regimes of the Spokane River: spring high flow, summer low flow, and winter moderate flow. Surface water samples will cover a 24-to 36-hour period giving a better temporal average than with a single grab sampling event. Sediment traps will be deployed, retrieved, and analyzed during each of the 3 flow regimes, but they will be present in the river year-round. This allows for averaging results to represent annual conditions.

### **6.2.2.3 Completeness**

The data for this project will be considered complete if 95% of the planned samples were collected and analyzed acceptably.

## 7.0 Sampling Process Design (Experimental Design)

### 7.1 Study Design

PCBs, PBDEs, dioxins/furans, and metals are contaminants of concern (COCs) for the Spokane River. Cleanup activities and monitoring for these COCs is ongoing but has mostly been focused in areas upstream of the Lake Spokane Dam. This project will focus on establishing a long-term monitoring station for COCs downstream of Lake Spokane near the upper Spokane Tribal boundary.

Ecology's Environmental Assessment Program (EAP) will establish the long-term monitoring station. Surface water and suspended sediments will be monitored for COCs during the 3 major hydrologic regimes annually for the river: spring high flow, summer low flow, and winter moderate flow. The monitoring schedule is shown in Table 6 and discussed in Section 5.4.

The first year of monitoring for the Spokane River long-term station will be included in a larger effort by EAP to assess the precision and accuracy of various types of high volume techniques for collecting low-level organics in surface water with a special focus on PCBs. The QA Project Plan for the high-volume collection techniques study is currently under development. Because the Spokane River long-term station will be included in this larger effort, both CLAM and 20-liter composite samples will be used to measure for PCBs and PBDEs for the first year of monitoring. In subsequent years, surface water monitoring at the long-term station will likely focus on a single high-volume collection method, such as the CLAM, that can be used to evaluate trends in the Spokane River.

A higher number of field replicate samples and laboratory QA/QC samples will be analyzed during the first year of monitoring, especially for PCBs. Fewer QA/QC samples should be needed for all COCs in subsequent years. Questions about the precision and accuracy of the chosen high volume collection technique will have been answered through both the first year of monitoring for the long-term station as well as through the high volume collection methods validation study.

High-resolution methods will be used to analyze for PCBs (EPA 1668c), PBDEs (EPA 1614) in surface water and suspended sediments. Suspended sediments will also be analyzed for dioxins and furans (EPA 1613b). These high-resolution methods allow for the lowest detection limits available and can detect for as many of the 209 congeners as possible for both PCBs and PBDEs. Having full congener data gives more information and allows for future "finger-printing" and source tracing. Much of the recent monitoring conducted by The SRRTTF and others in the Spokane River watershed includes the use of EPA 1668c for measuring PCBs.

### 7.1.1 Field measurements

Surface water measurements will be taken at the same time as surface water samples. A MiniSonde hydrolab will be used to collect the following parameters:

- Temperature
- pH
- Conductivity
- Dissolved Oxygen

The starting and ending flow rates for the CLAM samplers will be recorded. These volumetric measurements are used to estimate the total volume of water sampled by the CLAMs. A totalizer from the CLAM manufacturer will also be used to get a more accurate recording of the total volume sampled. More information on the use of CLAMs in the field is available in Appendix B.

### 7.1.2 Sampling location and frequency

Surface water will be sampled at either the Avista Park site on the south bank of the river or the UGM site on the north side of the river upstream of the Chamokane River confluence with the Spokane River (Figure 6). The UGM site is the first choice for sampling, due to its location just upstream of the upper Spokane Tribal border. This is the location where the Spokane Tribe takes water measurements with their hydrolab and it may have better security than the Park site does. Sediment traps will be deployed in the slack water area downstream of the Highway 231 bridge (Figure 6).

The flow regime for the Spokane River falls into 3 major hydrologic regimes: (1) spring high flow, (2) summer base or low flow and (3) winter moderate flow. Figure 2 shows the historical flow regime for the river and the 3 major flow regimes. Surface water and suspended sediment sampling will occur during each of the 3 major river conditions.

The sampling schedule for the project is shown in Table 6. The first surface water sampling (using both CLAM collection device and 20-liter composite samples) will occur in early May 2015 and again in August 2015 and January 2016. Sediment traps for collecting suspended sediment will be deployed 3 times a year for 4 months at a time. The first deployment is slated for late April 2015. The long-term plan is for this schedule of sampling to occur on an annual basis.

### 7.1.3 Parameters to be determined

- Surface Water
  - Dissolved Organic Carbon (DOC)
  - Total Organic Carbon (TOC)
  - Total Suspended Solids (TSS)
  - Total Non-Volatile Suspended Solids (TNVSS)
  - Hardness
  - Cadmium, copper, lead, and zinc (low-level, total, and dissolved phase)

- PCB congeners
- PBDEs
- Suspended Sediments
  - Percent solids
  - TOC
  - Cadmium, copper, lead, and zinc
  - PCB congeners
  - PBDEs
  - Dioxins and furans

## 7.2 Maps or diagram

A map of the Washington portion of the Spokane River watershed is shown in Figure 1. A map with the proposed sampling locations is shown in Figure 6. Surface water will be sampled at either the Avista Park site on south bank of the river or the UGM site on the north side of the river above the Chamokane River confluence with the Spokane River.

## 7.3 Assumptions underlying design

There is an assumption that with using high-volume collection methods and low-level analyses, that PCBs and PBDEs will be detected at the required reporting limits for the project =1.0 (for PCBs) and 10-100 (for PBDEs) pg absolute per extract of 20 or more liters of surface water.

There is also an assumption that sediment traps will work in the section of Spokane River between Long Lake Dam and the Spokane Tribal border. Depth and current are major factors for successful deployment and retrieval of sediment traps.

## 7.4 Relation to objectives and site characteristics

Not applicable.

## 7.5 Characteristics of existing data

There is a lack of surface water and sediment data for toxics for the section of river to be monitored in this study. Recent fish tissue data (2012) suggests that concentrations of PCBs, PBDEs, and dioxins and furans near the study site are low compared to areas sampled upstream (Seiders et al., 2014).



## 8.0 Sampling Procedures

### Surface Water Monitoring

CLAMs will be deployed for 24-36 hours at the long-term station. Including replicates, there will be 4 CLAMs deployed during each sampling event. At deployment and again at retrieval, half the amount of surface water will be collected and transferred into the appropriate sample containers in order to complete a composite sample. The hardness and metals samples will be conducted as grab samples and will be collected once at deployment and then sampled a second time at retrieval. See Table 13.

Table 13. Surface Water Collection Methods.

Parameters	Collection Method	24 - 36 hours		
PCBs & PBDEs	CLAM	deploy	————> —————>	retrieve
PCBs & PBDEs	20 Liter	1/2 fill	for composite	1/2 fill
DOC, TOC, TSS and TNVSS	specific bottle	1/2 fill	for composite	1/2 fill
Hardness and metals	Grabs	sample		sample

Following the procedure outlined in the SOP EAP003, *Sampling of Pesticides in Surface Waters, Version 2.1* (Anderson, 2012), we will use clean jars for compositing. Compositing jars will be acquired from the laboratories. The contract laboratory requires proof of the compositing jars' and 20 liter carboys' cleanliness for analysis of PCBs and PBDEs. For transferring into the DOC, TOC, and TSS/TNVSS bottles, an organics-free, certified, narrow-mouth 1-liter jar from MEL will be used.

Figure 7 shows the types and numbers of SPE disks to be used for CLAM and 20 liter samples. All the SPE disks will be analyzed for PCBs and PBDEs. There will be 3 CLAM replicate samples. Two of the 3 samples will have an additional SPE disk for assessment of breakthrough. The first SPE in this 2-disk CLAM sample will be spiked with a field spiking solution and the second disk will not have the field spiking solution. Analysis of both of these SPE disks will allow for an assessment of breakthrough or wash-off of the field spiked labeled compounds and the native PCBs and PBDEs. The field spiking solution will consist of the following labeled compounds:  $^{13}\text{C}$ -PCB-31,  $^{13}\text{C}$ -PCB-95,  $^{13}\text{C}$ -PCB-153 and  $^{13}\text{C}$ 12-2,2',3,4,4',6-HxBDE.

The 20-liter samples will be filtered and extracted at the contract laboratory using the same SPE disks as with the CLAM samples. These SPEs will also be spiked with the field spiking solution.

Deployment and retrieval methods for the CLAM are described in detail in Appendix B.

Disk Type	Analysis	Collection Method	Replicate No.
○	PCBs/PBDEs	CLAM #1	1
○ ○	PCBs/PBDEs	CLAM #2	2
○ ○	PCBs/PBDEs	CLAM #3	3
○	PCBs/PBDEs	20 L --> SPE	1
○	PCBs/PBDEs	20 L --> SPE	2

○ C-18 SPE disk (with field spiking solution)

○ C-18 SPE disk (without field spiking solution)

Figure 7. CLAM Deployment Set-up.

## Sediment Traps

Sediment traps will be deployed in duplicate at the long-term monitoring station. Each trap holds 2 collection cylinders, for a total of 4 cylinders in each reservoir. Deploying 2 traps has several benefits:

- With low sediment rates, more cylinders means more material can be collected.
- There is a backup sampler in case something happens to one of the traps.
- Coverage in 2 locations can be more representative as hydrology can vary even in short distances.

The sediment trap cylinders will be swapped out after 4 months of deployment. New cylinders will then be deployed for another 4 months. This will allow for sedimentation rates to be calculated for 3 separate 4-month deployment periods and characterized on an annual basis.

The EAP's standard sediment trap deployment method for reservoirs and deep water is to suspend a trap in the middle of the water column with an anchor, snag line, and hardball float. This method is described in detail in Norton (1996) and a schematic of the sediment trap design and deployment configuration is displayed in Figure 8. The hardball float sits 6 feet below the water surface so that it can stay taut with fluctuating water levels and so it's not disturbed by vessel traffic or floating debris. The trap is then retrieved by dragging a hook to grab the snag line underwater.

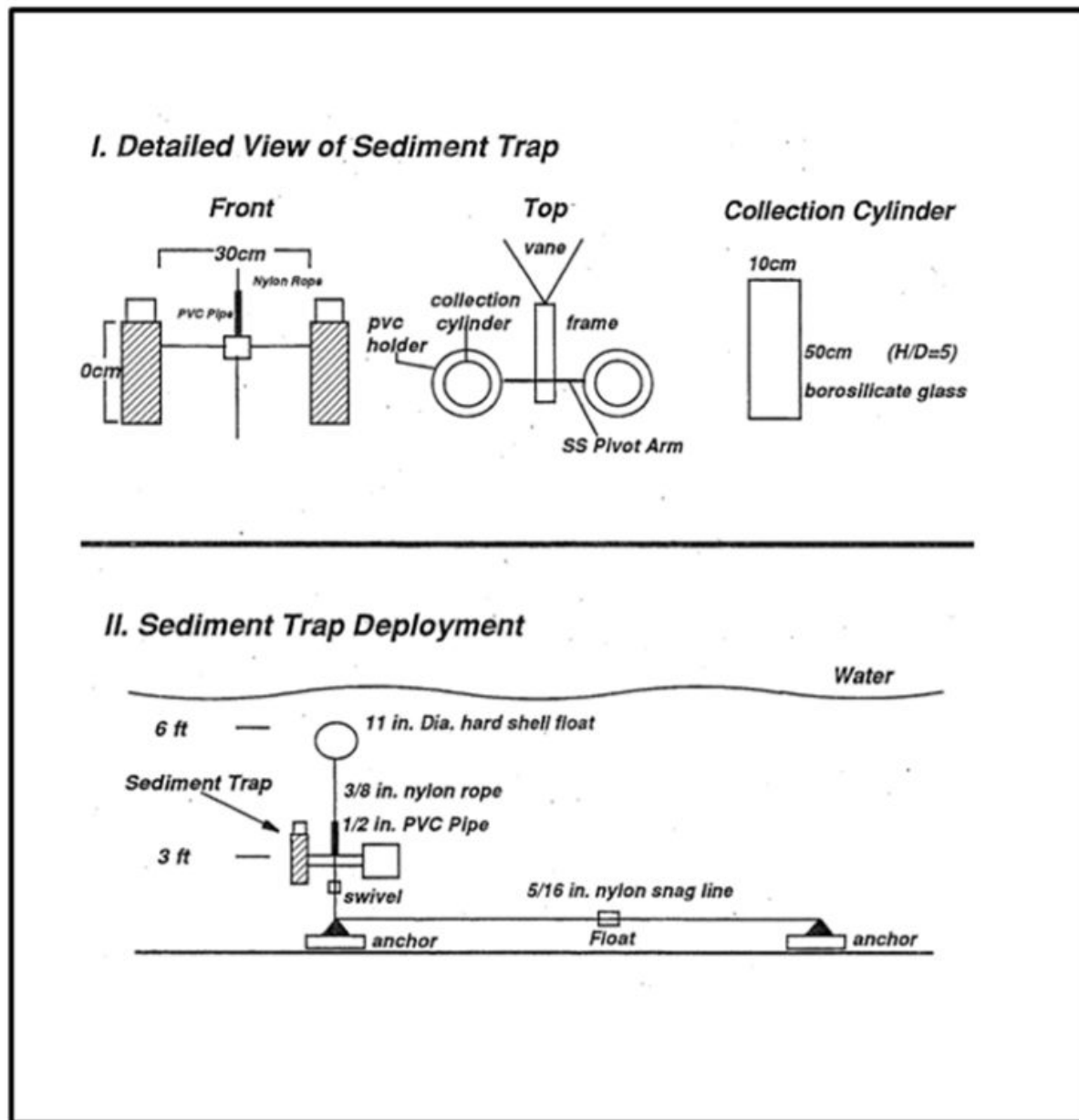


Figure 8. Schematic of Sediment Trap Design and Deployment Configuration (Norton, 1996).

Each sediment trap holds two glass collection cylinders each with a collection area of 78.5 cm<sup>2</sup> and a height-to-width ratio of 5. This same type of trap was successfully used in the Spokane River at Upriver Dam and Ninemile Dam in the fall of 2012 (Era-Miller, 2014).

Before deployment, cylinders will be cleaned with Liquinox soap and hot water, followed by 10% nitric acid, and then rinsed with deionized water. Cylinders will then be rinsed with pesticide-grade acetone and finally hexane. This procedure is covered in more detail in SOP EAP090 – *Decontaminating Field Equipment for Sampling Toxics in the Environment* (Frieze, 2014). During transport to the field, the tops of each cylinder will be covered with clean aluminum foil.

At deployment, the cylinders are partially filled with high salinity water (4% sodium chloride – NaCl), which contains mercuric chloride (HgCl) as a preservative to reduce microbial degradation of the samples. The recipe for the preservative solution is 15 grams of HgCl and 300 to 400 grams of NaCl to 15 liters of deionized water.

## 8.1 Field measurement and field sampling SOPs

The following Ecology Standard Operating Procedures (SOPs) will be used for this project:

- EAP003 – *Sampling of Pesticides in Surface Waters, Version 2.1* (Anderson, 2012).
- EAP015 – *Manually Obtaining Surface Water Samples, Version 1.2* (Joy, 2013).
- EAP029 – *Collection and Field Processing of Metals Samples, Version 1.5* (Ward, 2015).
- EAP033 – *Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0* (Swanson, 2007).
- EAP070 – *Minimizing the Spread of Invasive Species* (Parsons et al., 2012).
- EAP090 – *Decontaminating Field Equipment for Sampling Toxics in the Environment* (Frieze, 2014).

## 8.2 Containers, preservation methods, holding times

Sampling containers, preservation, and holding times are shown in Table 14. Information for analyses being conducted at MEL was adapted from the Manchester Laboratory User's Manual and through conversations with MEL and the contract laboratories (MEL, 2008).

Table 14. Sample Containers, Preservation, and Holding Times.

Parameter	Matrix	Container	Preservation	Holding Time
DOC	Surface Water (20 L)	125 mL pre-acidified poly bottle	Filter in field with 0.45 um pore size filter; 1:1 HCl to pH<2; Cool to 6°C	28 days
TOC		125 mL pre-acidified poly bottle	1:1 HCl to pH<2; Cool to 6°C	
TNVSS		1 L poly bottle	Cool to 6°C	7 days
Hardness*		125 mL poly bottle	1:1 HNO3 to pH<2	6 months after preservation
Metals: Cu, Cd, Pb & Zn*		500 mL pre-acidified HDPE bottle	Field filter for dissolved; 1:1 HNO3 to pH<2	6 months after preservation
PCB congeners		20 L carboy or canister	Cool to 6°C	1 year
PBDEs				
PCB congeners	Surface Water (CLAM)	The self-contained C-18 SPE disks are placed in amber plastic bags provided by the manufacturer	Cool to 6°C	14 days
PBDEs				
Percent Solids	Suspended Sediments	From same jar as particulate organics (4-oz jar)	Cool to 6°C	7 days or 6 months frozen
TOC		Certified 2-oz amber glass w/ Teflon lid liner		14 days or 6 months frozen
Cu, Cd, Pb & Zn		Certified 4-oz amber glass w/ Teflon lid liner	Transport at 6°C; can store frozen at -18°C	6 months or 2 years frozen
PCB congeners				1 year extraction; 1 year analysis
PBDEs				
Dioxins/furans				

\* Hardness and metals collected as grab samples.

## 8.3 Invasive species evaluation

Field personnel for this project are required to be familiar with and follow the procedures described in SOP EAP070, *Minimizing the Spread of Invasive Species*.

The Spokane River watershed is considered to be an area of moderate concern. Because all monitoring for the project will occur in the same stream segment, chances of carrying aquatic invasive Species (AIS) from one part of the basin to another will be greatly reduced.

## 8.4 Equipment decontamination

Glass cylinders used in the sediment traps will be cleaned according to Ecology's SOP EAP090, *Decontamination of Sampling Equipment for Use in Collecting Toxic Chemical Samples*. Before deployment, cylinders will be cleaned with Liquinox soap and hot water, followed by 10% nitric acid, and then rinsed with deionized water. Cylinders will then be rinsed with pesticide-grade

acetone and finally hexane. During transport to the field, the tops of each cylinder will be covered with clean aluminum foil.

Proof of cleanliness of the compositing jars and 20-liter carboys for analysis of PCBs and PBDEs will be required by the contract laboratory.

CLAMs are clean and ready for use when they arrive from the contractor. Surface water is filtered through single-use SPE disks that are specifically cleaned as part of the conditioning process by the contract laboratory.

## **8.5 Sample ID**

Sample numbers will be assigned by MEL by way of a work order number for each monitoring event. Sample numbers will follow chronologically after the work order number (e.g., 1501027 - 1, 1501027 -2, etc.). Sample IDs will be assigned by the project manager for each sampling event prior to collection.

## **8.6 Chain-of-custody, if required**

Chain of custody will be maintained for all samples throughout the project.

## **8.7 Field log requirements**

Field data will be recorded in a bound, waterproof notebook on Rite in the Rain paper. Corrections will be made with single line strikethroughs, initials, and date.

The following information will be recorded in the project field log:

- Name and location of project
- Field personnel
- Sequence of events
- Any changes or deviations from the QA Project Plan
- Environmental conditions
- Date, time, location, ID, and description of each sample
- Field instrument calibration procedures
- Field measurement results
- Identity of QC samples collected
- Unusual circumstances that might affect interpretation of results

## **8.8 Other activities**

Not Applicable. Necessary activities are detailed in other sections of this QA Project Plan.

## **9.0 Measurement Methods**

### **9.1 Field procedures table/field analysis table**

Field data will be measured using a MiniSonde multi-meter following guidance in SOP EAP033 – Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0 (Swanson, 2007).

Field parameters for the project include:

- Temperature
- pH
- Conductivity
- Dissolved Oxygen

## 9.2 Lab procedures table

Table 15. Laboratory Methods and Sample Information.

Analyte	UOM	No. of Samples	No. of QA Samples	Total No. of Samples	Expected Range of Results	Laboratory Reporting Limits	Analytical Method
Surface Water (20 Liters)							
PCB Congeners	pg per sample	6	6	12	0.5 - 50 per cong.	1	EPA 1668c
PBDEs		6	6	12	5 -10,000 per cong.	10 - 100	EPA 1614
DOC		3	3	6	1 - 2	1	SM 5310B
TOC		3	3	6	1 - 2	1	
TNVSS		3	3	6	1 - 10	1	
TSS		3	3	6	1 - 10	1	SM 2540D
Hardness		6	6	12	25 - 100	0.3	SM 2340B
Copper	mg/L	12	9	21	0.5 - 1	0.1	EPA 200.8
Cadmium		12	9	21	0.04 - 0.2	0.02 (diss) 0.1 (total)	
Lead		12	9	21	0.05 - 2	0.02 (diss) 0.1 (total)	
Zinc		12	9	21	5 - 50	1 (diss) 5 (total)	
Surface Water (CLAM)							
PCB Congeners	pg per sample	15	9	24	0.5 - 50 per cong.	1	EPA 1668c
PBDEs		15	9	24	5 -10,000 per cong.	10 - 100	EPA 1614
Suspended Sediments							
PCB Congeners	ng/Kg dry weight	3	3	6	0.5 - 1500 per cong.	0.1*	EPA 1668c
PBDEs		3	3	6	0.5 - 25,000 per cong.	1 - 10*	EPA 1614
Dioxins/furans		3	3	6	0.2 - 300 per cong.	0.05*	EPA 1613c
Copper	mg/Kg dry weight	3	3	6	0.1 - 10	0.1	EPA 200.7 & Standard Methods
Cadmium		3	3	6	0.5 - 20	0.01	
Lead		3	3	6	10 - 500	0.1	
Zinc		3	3	6	100 - 2000	5	
Solids	%	3	3	6	20 - 40 %	1%	SM 2540G
TOC		3	3	6	1 - 15 %	0.1%	PSEP TOC

† reporting limit for BDE 209 is 200 pg per sample

\* based on a 10 gram sample

UOM: unit of measurement

PSEP: Puget Sound Estuary Program

SM: Standard Methods

diss: dissolved phase



### 9.2.1 Analyte

- DOC
- TOC
- Hardness
- TNVSS
- TSS
- Percent Solids
- Metals (cadmium, copper, lead, and zinc)
- PCB congeners
- PBDEs
- Dioxin and furans

### 9.2.2 Matrix

- Surface water
  - collected via 20 liter or 1 gallon compositing
  - collected via CLAM
  - collected as single grab samples (metals only)
- Suspended sediments

### 9.2.3 Number of samples

See Table 15.

### 9.2.4 Expected range of results

See Table 15.

### 9.2.5 Analytical method

See Table 15.

### 9.2.6 Sensitivity/Method Detection Limit (MDL)

For the EPA 1600 series methods for PCBs, PBDEs, and dioxin/furans, the reporting limits shown in Table 15 are the estimated detection limits (EDLs). The reporting limits shown for the rest of parameters are the MDLs as reported by MEL.

## 9.3 Sample preparation method(s)

For the EPA 1600 series methods for PCBs, PBDEs, and dioxin/furans, the preparation and extraction methods are described in the analytical methods. However, for the CLAM and 20-liter surface water samples, the same type of SPE disk will be used during extraction. More information on the specifics of CLAM SPE extraction can be found in Appendix B.

## **9.4 Special method requirements**

The use of CLAM and 20 liters for surface water sample collection for low-level analysis will require special coordination with the contract laboratory. The project manager, Karin Feddersen from MEL, who manages and reviews contracts with the contract laboratories, and Brent Hepner (from C.I.Agent – the CLAM manufacturer) will have a conference call with contract laboratory conducting the high resolution methods for the CLAM and 20 liter water samples shortly after the bid for the laboratory analysis is awarded. The purpose of the meeting will be to discuss specific methods for SPE disk conditioning, field spiking and eluting, as well logistics for collection and transport of the 20-liter samples.

## **9.5 Lab(s) accredited for method(s)**

All laboratories for the project will be accredited, and all the analyses will be standard published methods.

## 10.0 Quality Control (QC) Procedures

### 10.1 Table of field and lab QC required

Table 16. Field and Laboratory QC Samples.

Parameter	Lab Control Sample	Method Blank	Surrogate Recoveries	OPR Standards	MS/MSD	Lab Duplicate Analysis	Field Duplicate Analysis	Filter Blank	Travel Blank	Field Transfer Blank
<i>20 Liter, 1 gallon and grabs</i>										
DOC & TOC	1/batch	1/batch	--	--	1/batch	1/batch	1/batch	--	--	--
TSS & TNVSS	1/batch	1/batch	--	--	--	1/batch	1/batch	--	--	--
Hardness	1/batch	1/batch	--	--	1/batch	1/batch	1/batch	--	--	1/batch
Metals <sup>†</sup>	1/batch	1/batch	--	--	1/batch	2/batch	1/batch	1/batch	--	1/batch
PCBs	1/batch	1/batch	all samples	all samples	--	--	1/batch	1/batch*	1/batch	1/batch
PBDEs	1/batch	1/batch	all samples	all samples	--	--	1/batch	1/batch*	1/batch	1/batch
<i>CLAM</i>										
PCBs	1/batch	1/batch	all samples	all samples	--	--	1/batch	1/batch*	--	1/batch
PBDEs	1/batch	1/batch	all samples	all samples	--	--	1/batch	1/batch*	--	1/batch
<i>Suspended Sediments</i>										
TOC	1/batch	1/batch	--	--	1/batch	1/batch	1/batch	--	--	--
Metals	1/batch	1/batch	--	--	1/batch	1/batch	1/batch	--	--	--
PCBs	1/batch	1/batch	all samples	all samples	--	1/batch	1/batch	--	--	--
PBDEs	1/batch	1/batch	all samples	all samples	--	1/batch	1/batch	--	--	--
Dioxins/furans	1/batch	1/batch	all samples	all samples	--	1/batch	1/batch	--	--	--

Batch: One sampling event (3/yr)

OPR: Ongoing Precision and Recovery

MS/MSD: Matrix Spike and Matrix Spike Recovery

<sup>†</sup> Field duplicate and transfer blank will be conducted on the total sample; filter blank conducted on the dissolved sample; and the laboratory duplicate analysis will be conducted on both.

\*Filter blanks for 20 liter and CLAM samples will consist of analysis of a clean SPE disks in the laboratory.

The QC samples shown in Table 16 have MQOs associated with them as described in Section 6.2. These criteria must be met to obtain fully usable data.

#### Background Contamination from SPE Disk current

In order to address potential background contamination from the SPE disks, clean and pre-conditioned SPE disks will be extracted, analyzed, and reported for PCBs and PBDEs in the same manner as field samples. Two EAP studies currently underway in the Little Spokane River (Frieze and Coots, 2014) and Wenatchee River (Hobbs, 2014a) along with the upcoming high-volume collection techniques study will also entail analysis of SPE disks for possible background contamination from PCBs. In addition, SPE disks for these studies and the Spokane Long-Term Station were obtained from the same batch upon manufacture so that data from the

blank SPE disks will be comparable between studies and can be pooled to better characterize potential contamination from SPE disks.

## **10.2 Corrective action processes**

The laboratory analysts will document whether project data meets method QC criteria. Any departures from normal analytical methods will be documented by the laboratory and described in the data package from the laboratories and also in the final report for the project.

To avoid splitting the surface water sample extracts and raising reporting limits, archive samples will not be saved for the May 2015 sampling event. If a significant number of analytical results fall outside established MQOs, then the laboratory analyst and the project manager will decide what changes will need to occur for the surface water sampling events in August and January so that QC criteria are met. Sediment samples will be archived if re-analysis is needed.

## **11.0 Data Management Procedures**

### **11.1 Data recording/reporting requirements**

Field data will be recorded in a bound, waterproof notebook on Rite in the Rain paper. Corrections will be made with single line strikethroughs, initials, and date. Data will be transferred to Microsoft Excel for creating data tables and figures and for basic statistical analysis.

### **11.2 Laboratory data package requirements**

MEL's standard data deliverable package will be adequate for this project and the data deliverables required by the contract laboratory will be detailed in the bid solicitation for the contract laboratory work.

### **11.3 Electronic transfer requirements**

MEL has an EDD (electronic data deliverable) that is compatible with EIM data requirements and that will meet the requirements of this project. The contract laboratory will also have an EDD that meets the requirements of this project. These requirements will be detailed in the bid solicitation for the contract laboratory work.

### **11.4 Acceptance criteria for existing data**

All existing data is stored in EIM and as such is acceptable for use as described under the data quality descriptions in EIM.

### **11.5 EIM/STORET data upload procedures**

All completed project data will be entered into Ecology's Environmental Information Management (EIM) database for availability to the public and interested parties, with the exception of the surface water data generated using CLAM. CLAM is still in the developmental phase. Until standard operating procedures have been approved for the CLAM, data will not be entered into EIM.

Data entered into EIM follow a formal data review process where data are reviewed by the project manager, the person entering the data, and an independent reviewer.

EIM can be accessed on Ecology's Internet homepage at [www.ecy.wa.gov](http://www.ecy.wa.gov). The project will be searchable under Study ID BERA0012.

## **12.0 Audits and Reports**

### **12.1 Number, frequency, type, and schedule of audits**

MEL participates in performance and system audits of their routine procedures. The results of these audits are available on request. The contract laboratories are also routinely audited as part of their internal procedures and as part of their accreditation.

### **12.2 Responsible personnel**

MEL chemists and the project manager will be responsible for review of the data packages. The Quality Assurance Coordinator for MEL, Karin Feddersen, will carry out the review of the contract laboratory data packages.

### **12.3 Frequency and distribution of report**

A report will be written after data from the first year are collected and analyzed for this project. However, we expect to continue monitoring to evaluate long-term trends.

After the draft report is reviewed by the client for the project, Ecology Eastern Regional Office Water Quality Program (ERO WQP), it will be sent to the Spokane River Regional Toxics Task Force (SRRTTF) and Spokane Tribe of Indians for their reviews.

### **12.4 Responsibility for reports**

Brandee Era-Miller, project manager and principal investigator, will write a final report for the first year of monitoring at the Spokane River long-term station. Data from the first year of monitoring at the long-term station will also be included in a larger report assessing various high-volume surface water collection techniques for low-level organics. This report will be written by EAP staff William Hobbs and published in 2017. In addition, data from the first year of monitoring at the long-term station will be used to help develop a standard operating procedure (SOP) for use of CLAM samplers by EAP. EAP staff Michael Friese will write the SOP.

## **13.0 Data Verification**

### **13.1 Field data verification, requirements, and responsibilities**

Data verification for all field-generated data will be conducted by the project manager.

### **13.2 Lab data verification**

Data verification for all laboratory data will be conducted by the project manager. Karin Feddersen, the Quality Assurance Officer at MEL, will review and verify data from the contract laboratories.

### **13.3 Validation requirements, if necessary**

Third party data validation will not be required for this project.

## 14.0 Data Quality (Usability) Assessment

### 14.1 Process for determining whether project objectives have been met

The project manager will determine if the project data is useable by assessing whether the data have met the MQOs outlined in Table 12. Based on this assessment, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

### 14.2 Data analysis and presentation methods

Not applicable.

### 14.3 Treatment of non-detects

Non-detected data (data with a “U” or “UJ” flag designated by the lab) will not be used for summation of total results, homologue groups, or calculation of Toxic Equivalencies (TEQs) for dioxins and furans.

For summing of totals, non-detected results will be assigned a value of zero. If only non-detected results comprise a total value, then the final total result was simply reported as “ND” for not detected. Sample totals will be assigned a qualifier of “J” (estimated) if more than 10% of the result concentrations are composed of results containing “J” qualifiers.

#### Data Qualifier Definitions

- U The analyte was not detected at or above the reported sample quantitation limit.
- UJ The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.
- J The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
- NJ The analyte has been “tentatively identified” and the associated numerical value represents its approximate concentration.
- ND Not Detected.

### Censoring for Method Blank Contamination

For high-resolution methods (EPA 1600 series for PCBs, PBDEs, and dioxins/furans), individual congener results will be considered non-detects (“U” or “UJ”) if the concentrations are less than 3 times the concentration of the associated laboratory method blanks. The result values (qualified as non-detects) will then be reported at the estimated quantitation limit (EQL) or at the level of detection, whichever is higher.



## Censoring for Tentatively Identified Analytes

Results for the high-resolution methods that do not meet the isotopic abundance ratio and retention time criteria for positive identification will be qualified by MEL with an “NJ” and considered to be tentatively identified. For reporting purposes, the project manager will censor all “NJ” qualified data by assigning a qualifier of “UJ” and using a result value at the estimated quantitation limit (EQL) or at the level of detection, whichever is higher.

### 14.4 Sampling design evaluation

Sampling and collection methods for the project are designed to be time-integrated such that seasonal averages will be possible to determine. If the project as currently designed yields acceptable data, then the data can be used to characterize one year of seasonal toxics data for the monitoring site. Several more years of data will be needed to accurately determine long-term trends at the monitoring site.

### 14.5 Documentation of assessment

This will occur in the final report.

## 15.0 References

Anderson, P., 2012. Standard Operating Procedure for Sampling of Pesticides in Surface Waters, Version 2.1. Washington State Department of Ecology, Olympia, WA. SOP Number EAP003. [www.ecy.wa.gov/programs/eap/quality.html](http://www.ecy.wa.gov/programs/eap/quality.html)

Butkus, S. and K. Merrill, 1999. Spokane River Dissolved Metals Total Maximum Daily Load – Submittal Report. Washington State Department of Ecology, Olympia, WA. Publication No. 99-49. <https://fortress.wa.gov/ecy/publications/SummaryPages/9949.html>

Crossley, Brian, 2015. Spokane Tribe of Indians. Personal Communication.

DOH, 2009. Spokane River Fish Advisory. Washington State Department of Health and the Spokane Regional Health District. DOH 334-164. <http://www.doh.wa.gov/Portals/1/Documents/Pubs/334-164.pdf>

EAP, 2014. Environmental Assessment Program Safety Manual – 2012 (*revised September 2014*). The Environmental Assessment Program, Washington State Department of Ecology, Olympia, WA.

Ecology, 2012. Water Quality Program Policy 1-11: Assessment of Water Quality for the Clean Water Act Section 303(d) and 305(b) Integrated report. Washington State Department of Ecology, Olympia, WA.

Era-Miller, B., 2014. Technical Memo: Spokane River Toxics Sampling 2012-2013 – Surface Water, CLAM and Sediment Trap Results. Technical memo to Adriane Borgias, Washington State Department of Ecology, Water Quality Program, Eastern Regional Office, Spokane Washington from Brandee Era-Miller, Washington State Department of Ecology, Environmental Assessment Program. Memo dated May 30, 2014.

Friese, M., 2014. Standard Operating Procedure for Decontaminating Field Equipment for Sampling Toxics in the Environment. Washington State Department of Ecology, Olympia, WA. SOP Number EAP090. [www.ecy.wa.gov/programs/eap/quality.html](http://www.ecy.wa.gov/programs/eap/quality.html)

Friese, M. and R. Coots, 2014. Quality Assurance Project Plan: Little Spokane River PCBs in Fish Tissue Verification Study. Washington State Department of Ecology, Olympia, WA. Publication No. 14-03-127. <https://fortress.wa.gov/ecy/publications/SummaryPages/1403127.html>

Hobbs, W., 2014a. Quality Assurance Project Plan: Wenatchee River PCB and DDT Source Assessment. Washington State Department of Ecology, Olympia, WA. Publication No. 14-03-117. <https://fortress.wa.gov/ecy/publications/SummaryPages/1403117.html>

Hobbs, W., 2014b. Quality Assurance Project Plan: Pine Creek Toxaphene Source Assessment. Washington State Department of Ecology, Olympia, WA. Publication No. 14-03-107. <https://fortress.wa.gov/ecy/publications/SummaryPages/1403107.html>

Hopkins, B., D. Clark, M. Schlender, and M. Stinson, 1985. Basic Water Monitoring Program Fish Tissue and Sediment Sampling for 1984. Washington State Department of Ecology, Olympia, WA. Publication No. 85-7.

<https://fortress.wa.gov/ecy/publications/summarypages/857.html>

Joy, J., 2013. Standard Operating Procedure for Manually Obtaining Surface Water Samples, Version 1.2. Washington State Department of Ecology, Olympia, WA. SOP Number EAP015. [www.ecy.wa.gov/programs/eap/quality.html](http://www.ecy.wa.gov/programs/eap/quality.html)

MacInnis, J., B. Lackaff, R. Beose, G. Stevens, S. King, and R. Lindsay, 2009. The Spokane Valley-Rathdrum Prairie Aquifer Atlas 2009 Update. Spokane Washington, City of Spokane.

MEL, 2008. Manchester Environmental Laboratory Lab Users Manual, Ninth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

MEL, 2012. Manchester Environmental Laboratory Quality Assurance Manual. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

Norton, D., 1996. Commencement Bay Sediment Trap Monitoring Program. Washington State Department of Ecology, Olympia, WA. Publication No. 96-315. <https://fortress.wa.gov/ecy/publications/summarypages/96315.html>

Parsons, J., 2012. Standard Operating Procedure for Minimizing the Spread of Invasive Species. Washington State Department of Ecology, Olympia, WA. SOP Number EAP070. [www.ecy.wa.gov/programs/eap/quality.html](http://www.ecy.wa.gov/programs/eap/quality.html)

Seiders, K., C. Deligeannis, P. Sandvik, and M. McCall, 2014. Freshwater Fish Contaminant Monitoring Program: 2012 Results. Washington State Department of Ecology, Olympia, WA. Publication No. 14-03-020. <https://fortress.wa.gov/ecy/publications/SummaryPages/1403020.html>.

Serdar, D., B. Lubliner, A. Johnson, and D. Norton, 2011. Spokane River PCB Source Assessment, 2003-2007. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-013. <https://fortress.wa.gov/ecy/publications/summarypages/1103013.html>.

Spokane Tribe of Indians, 2010. Spokane Tribe of Indians Surface Water Quality Standards. Resolution 2010-173. Spokane Tribe of Indians, Spokane, WA. February 25, 2010.

Swanson, T., 2007. Standard Operating Procedure for Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP033. [www.ecy.wa.gov/programs/eap/quality.html](http://www.ecy.wa.gov/programs/eap/quality.html)

WAC 173-201A. Water Quality Standards for Surface Waters in the State of Washington Washington State Department of Ecology, Olympia, WA. [www.ecy.wa.gov/laws-rules/ecywac.html](http://www.ecy.wa.gov/laws-rules/ecywac.html)

WAC 173-204. Sediment Management Standards. Washington State Department of Ecology, Olympia, WA. Revised February 2013, Effective September 2013. Publication No. 13-09-055. <https://fortress.wa.gov/ecy/publications/SummaryPages/1309055.html>

Ward, W.J., 2015. Standard Operating Procedure for the Collection and Field Processing of Metals Samples, Version 1.5. Washington State Department of Ecology, Olympia, WA. SOP Number EAP029. [www.ecy.wa.gov/programs/eap/quality.html](http://www.ecy.wa.gov/programs/eap/quality.html)

## 16.0 Figures

The figures in this QA Project Plan are inserted after they are first mentioned in the text.

## 17.0 Tables

The tables in this QA Project Plan are inserted after they are first mentioned in the text.

## 18.0 Appendices

## **Appendix A. 303(d) Listings for Toxics in the Spokane River**

Table A-1 shows all the water quality impairments and waters of concern for toxics parameters in the mainstem Spokane River including Lake Spokane. Not shown in Table A-1 are the listings for category 1 (meets tested criteria) and category 3 (insufficient data). Table A-2 gives the definitions for all the categories (1–5).



Table A-1. 303(d) Listings for Toxic Parameters in the Spokane River.

Listing ID	WRIAs	Waterbody Names	Proposed Category*	2008 Category	Parameter	Medium	Assessment Unit ID
51587	57 - Middle Spokane	SPOKANE RIVER	5	5	2,3,7,8-TCDD	Tissue	17010305000011
42411	54 - Lower Spokane	SPOKANE RIVER	5	5	2,3,7,8-TCDD	Tissue	17010307000774
51586	54 - Lower Spokane	SPOKANE RIVER	5	5	2,3,7,8-TCDD	Tissue	17010307009102
42410	54 - Lower Spokane	SPOKANE LAKE	5	5	2,3,7,8-TCDD	Tissue	4711716C1
78625	54 - Lower Spokane	SPOKANE RIVER	5	3	2,3,7,8-TCDD TEQ	Tissue	17010307009085
8201	57 - Middle Spokane	SPOKANE RIVER	5	5	PCB	Tissue	17010305000011
8202	57 - Middle Spokane	SPOKANE RIVER	5	5	PCB	Tissue	17010305000009
8207	57 - Middle Spokane	SPOKANE RIVER	5	5	PCB	Tissue	17010305000010
14397	57 - Middle Spokane	SPOKANE RIVER	5	5	PCB	Tissue	17010305000012
14400	54 - Lower Spokane	SPOKANE RIVER	5	5	PCB	Tissue	17010307009102
78968	54 - Lower Spokane	SPOKANE RIVER	5	3	PCB	Tissue	17010307009085
9027	54 - Lower Spokane	SPOKANE RIVER	5	5	PCB	Tissue	17010307000010
9033	54 - Lower Spokane	SPOKANE RIVER	5	5	PCB	Tissue	17010307000774
14385	54 - Lower Spokane	SPOKANE RIVER	5	5	PCB	Tissue	17010307009615
78928	54 - Lower Spokane	SPOKANE LAKE	5	3	PCB	Tissue	4711717B9
78929	54 - Lower Spokane	SPOKANE LAKE	5	3	PCB	Tissue	47117H5J8
78930	54 - Lower Spokane	SPOKANE LAKE	5	3	PCB	Tissue	4711715A4
78931	54 - Lower Spokane	SPOKANE LAKE	5	3	PCB	Tissue	4711717D3
78932	54 - Lower Spokane	SPOKANE LAKE	5	3	PCB	Tissue	4711715A5
78933	54 - Lower Spokane	SPOKANE LAKE	5	3	PCB	Tissue	4711717E2
9015	54 - Lower Spokane	SPOKANE LAKE	5	5	PCB	Tissue	4711717D4
9021	54 - Lower Spokane	SPOKANE LAKE	5	5	PCB	Tissue	47117H5I3
36440	54 - Lower Spokane	SPOKANE LAKE	5	5	PCB	Tissue	4711718C2
36441	54 - Lower Spokane	SPOKANE LAKE	5	5	PCB	Tissue	4711716C1
9057	57 - Middle Spokane	SPOKANE RIVER	4A	4A	Lead	Water	17010305000012
8213	57 - Middle Spokane	SPOKANE RIVER	4A	4A	Lead	Water	17010305000011
15552	57 - Middle Spokane	SPOKANE RIVER	4A	4A	Lead	Water	17010305000009
9046	54 - Lower Spokane	SPOKANE RIVER	4A	4A	Lead	Water	17010307009137
9043	54 - Lower Spokane	SPOKANE RIVER	4A	4A	Lead	Water	17010307009112
9045	54 - Lower Spokane	SPOKANE RIVER	4A	4A	Lead	Water	17010307010781
15322	54 - Lower Spokane	SPOKANE RIVER	4A	4A	Lead	Water	17010307007542
8200	57 - Middle Spokane	SPOKANE RIVER	4A	4A	Zinc	Water	17010305000012
8203	57 - Middle Spokane	SPOKANE RIVER	4A	4A	Zinc	Water	17010305000011
15553	57 - Middle Spokane	SPOKANE RIVER	4A	4A	Zinc	Water	17010305000009
9047	54 - Lower Spokane	SPOKANE RIVER	4A	4A	Zinc	Water	17010307009137
9031	54 - Lower Spokane	SPOKANE RIVER	4A	4A	Zinc	Water	17010307009112
9044	54 - Lower Spokane	SPOKANE RIVER	4A	4A	Zinc	Water	17010307010781
15335	54 - Lower Spokane	SPOKANE RIVER	4A	4A	Zinc	Water	17010307007542
15530	54 - Lower Spokane	SPOKANE LAKE	4A	4A	Zinc	Water	4711718D3
51639	57 - Middle Spokane	SPOKANE RIVER	2	2	2,3,7,8-TCDD TEQ	Tissue	17010305000009
51640	57 - Middle Spokane	SPOKANE RIVER	2	2	2,3,7,8-TCDD TEQ	Tissue	17010305000011
51638	54 - Lower Spokane	SPOKANE RIVER	2	2	2,3,7,8-TCDD TEQ	Tissue	17010307009102
13119	57 - Middle Spokane	SPOKANE RIVER	2	2	PCB	Water	17010305000010
14396	57 - Middle Spokane	SPOKANE RIVER	2	2	PCB	Water	17010305000011
9019	54 - Lower Spokane	SPOKANE LAKE	2	2	PCB	Water	4711718D3
9012	54 - Lower Spokane	SPOKANE LAKE	2	2	Aldrin	Water	4711718D3
9014	54 - Lower Spokane	SPOKANE LAKE	2	2	Chlordane	Water	4711718D3
9017	54 - Lower Spokane	SPOKANE LAKE	2	2	DDT	Water	4711718D3
9008	54 - Lower Spokane	SPOKANE LAKE	2	2	4,4'-DDD	Water	47117H5H4
9007	54 - Lower Spokane	SPOKANE LAKE	2	2	4,4'-DDE	Water	4711718D3
9013	54 - Lower Spokane	SPOKANE LAKE	2	2	Dieldrin	Water	47117H5H4
9030	54 - Lower Spokane	SPOKANE LAKE	2	2	Dieldrin	Water	4711718D3
9011	54 - Lower Spokane	SPOKANE LAKE	2	2	Endrin	Water	4711718D3
9009	54 - Lower Spokane	SPOKANE LAKE	2	2	Heptachlor	Water	47117H5H4
9010	54 - Lower Spokane	SPOKANE LAKE	2	2	Heptachlor Epoxide	Water	47117H5H4
11397	57 - Middle Spokane	SPOKANE RIVER	2	2	Mercury	Water	17010305000012
78441	54 - Lower Spokane	SPOKANE RIVER	2	3	Zinc	Water	17010307007531
8199	57 - Middle Spokane	SPOKANE RIVER	1	4A	Cadmium	Water	17010305000012

\*Proposed category is draft and subject to change. The proposed listings are currently undergoing public review and will require EPA approval before finalization.

Table A-2. State Water Quality Assessment Categories (Ecology, 2012)

Not impaired, or not known to be impaired	
Category 1. Meets Tested Criteria	EPA approval and TMDL not required
Category 2. Water of Concern	
Category 3. Insufficient Data	
Impaired	
Category 4. Impaired But Does Not Require a TMDL because: 4a. Has a TMDL approved by EPA 4b. Has a Pollution Control Plan 4c. Impaired by a Non-Pollutant	EPA approval and TMDL not required
Category 5. The 303(d) List	EPA approval and TMDL required

## Appendix B. Continuous low-level aquatic monitoring

*This information was taken from the Pine Creek Toxaphene Source Assessment Quality Assurance Project Plan (Hobbs, 2014b).*

The continuous low-level aquatic monitoring (CLAM) sampling device is a submersible, low-flow sampler that continuously and actively draws water through filtration and solid-phase extraction (SPE) media. The main supplier of the devices and the SPE disks used in this study is C.I.Agent (<http://www.ciagent-stormwater.com>). The pumps were commercially introduced in 2007, but the technology for SPE disks has been in laboratory use for the last 15 years under established EPA protocols (EPA3535A). Recent work by Coes et al. (2014) has documented the efficacy of CLAM devices when compared to both grab samples and passive samplers. Ecology has also begun using CLAM samplers on a more regular basis (Anderson and Sargeant, 2009; Coots, 2014; Hobbs, 2014a). However, there is no established SOP, and therefore the technique is still in trial.

### Solid-Phase Extraction (SPE) Disks

The CLAM device is simply a vessel for the SPE disk, which binds organic contaminants as water is pumped through. The pore size of the disks is 1.5 micrometers. The SPE media is specific to the contaminant of interest. C-18 extraction media is composed of a bonded silica filter with an octadecyl functional group that binds semi-volatile and non-volatile organic compounds (e.g., organochlorine pesticides, PCBs, and PAHs). The hydrophilic/lipophilic balanced (HLB) media uses a modified styrene polymer to effectively bind polar and non-polar compounds. The HLB disk has been used to sample many different pesticides, pharmaceuticals, and emerging contaminants.

The manufacturer of the CLAM device has conducted a retention and depletion bench study of the pump and the SPE disks for non-polar compounds. They found that there was excellent retention of spiked PAH and pesticide compounds in the disks following 100L of flushing with de-ionized water (DI) (Aqualytical, 2014; available at <http://www.ciagent-stormwater.com/documents/watermonitoring/RetentionandDepletionofIntegratedAnalytesintheCLAM.pdf>). The manufacturers of the SPE media and the lab suppliers have also conducted many retention studies for a variety of compounds.

The disks themselves are not directly handled by the lab or the field personnel. Disks are ordered and come contained in a sealed HDPE filter case with lure-locks at either end. Before deployment, the disks require conditioning with solvent, which rids the disk of any possible residual contamination. A complete step-by-step procedure is outlined in the manufacturer's laboratory application notes available online (<http://www.ciagent-stormwater.com/new-water-monitoring/>). The disks are cleaned with 50ml of dichloromethane (DCM), conditioned with 50ml of methanol, and rinsed with 50ml of reagent quality DI water. Residual DI water is left in the disk to maintain the pore space in the glass pre-filter that has been established by the conditioning rinse. The disks are capped and placed back in the foil pouch for shipment to the field. Conditioned disks can be kept refrigerated for up to 30 days; unconditioned disks are stable for up to a year.

## Deployment

The CLAM devices can be secured to suit the sample site. During deployment, the device must be carefully situated so that it does not obstruct the intake port. Typically in small streams the CLAM is positioned with the intake facing downstream, and the device is suspended at 2/3 the channel depth. In a shallow stream (such as Pine Creek) U-shaped rebar can be hammered into the streambed and the device suspended horizontally. In a deeper stream or lake, a concrete block with a float attached by cable and positioned just below the water surface can attach as a line to the CLAM (Anderson and Sargeant, 2009).

Before deployment, the flow rate of the device must be measured. Protocols describing a step-by-step method can be found at the manufacturer's website (<http://www.ciagent-stormwater.com/new-water-monitoring/>). The device is assembled and the battery pack is hooked up; this starts the internal pump. The device and extraction media are not compromised if the pump runs out of the water during set-up. A stainless steel bucket is filled with water from the site and the CLAM is placed in the bucket. Air is purged from the filter and then flow rate can be measured. A syringe is attached to the discharge port of the CLAM, with tubing, and the collected water volume is measured in the syringe and timed with a stopwatch. This procedure is repeated until the flow rate is consistent. The device can now be deployed and time of deployment recorded.

## Retrieval

The typical time of deployment for the CLAM is 12 to 36 hours. The device's battery pack limits the maximum time of deployment, and the water turbidity limits the minimum time of deployment. Suspended solids can slow flow rate by clogging the filter, ultimately stopping flow; this could result in a lost sample. Therefore, in turbid waters field personnel need to either return to the pump periodically to verify the pump is still running or deploy the pump for less time. There are no experimentally derived guidelines for time of deployment in turbid waters, since times vary dramatically with particle size and streamflow.

Before removing the device, personnel should take notes on its condition and exact time of retrieval. The flow rate of the CLAM is then measured as per the deployment. Currently, the user must then assume that the flow rate between the time of deployment and retrieval is linear. This flow rate is then used to calculate the total volume of water extracted over the period of deployment.

The following example illustrates this process. The CLAM is deployed at 1500 on March 3 and retrieved at 1200 March 4. The flow rate at deployment was  $50 \text{ ml min}^{-1}$  and at retrieval had decreased to  $20 \text{ ml min}^{-1}$ . The mean flow is therefore  $35 \text{ ml min}^{-1}$  and the total time of deployment is 21 hours. The total volume of water extracted is 44.1 L.

The CLAM is pulled from the water and disassembled at the site. The SPE disk is removed and placed back in the foil shipping pouch. The disks are placed in a cooler on ice until shipped directly to the lab. Refrigerated SPE disks have a holding time of 14 days.

## Analysis

SPE disks are shipped directly to the lab, accompanied by a standard chain of custody form. SPE disks are generally considered *other* as a matrix description and not water samples. While there is not an established SOP for the CLAM deployed SPEs, the contract lab should have an SOP for large volume extraction in the lab using similar or the same media. Established preparatory procedures should be in place from previous projects using CLAM samplers (J. Weakland, personal communication).

To analyze the total contaminant concentration bound to the SPE media, the lab must completely elute the deployed disks into separatory funnels. The disks are first rinsed with acetone to remove any water from the disk and then rinsed with dichloromethane to elute the disk. Before the DCM is added, the disk is spiked with a surrogate for laboratory QC of the separatory funnel extraction. The sample is concentrated using micro-Kuderna-Danish distillation under an N<sub>2</sub> atmosphere. The final extract volume is 1.0 mL. The extract is then run according to the methods pertaining to the contaminant of concern (e.g., GC/ECD in the case of toxaphene).

## Data Calculations and Reporting

The final quantified concentration is derived from the mass of the compound per milliliter of extract. The concentration of the compound in the sampled water is then calculated, based on the total volume of water pumped through the CLAM.

The following example illustrates this process. If the concentration of toxaphene in the extract is 5.05 ng mL<sup>-1</sup>, and the final volume of extract was 2.0 mL, there is 10.1 ng of toxaphene in the sample. If 44.1 L of water were sampled, as described earlier, the concentration is therefore 0.23 ng L<sup>-1</sup>.

Given that we are assuming the flow rate of the device is linear from deployment to retrieval, we can only consider the total water volume sampled to be an estimate. Therefore, the derived water concentration is an estimate and should be qualified as such.

C.I.Agent is currently developing a *totalizer* that will accurately measure the volume of water sampled with each CLAM. If proven successful as an effective volume measurement tool, analyte concentrations from the CLAM can be considered as accurate as any sample volume analyzed by the laboratory.

## Appendix C. Glossaries, Acronyms, and Abbreviations

### Glossary of General Terms

**Ambient:** Background or away from point sources of contamination. Surrounding environmental condition.

**Clean Water Act:** A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

**Conductivity:** A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

**Dissolved oxygen (DO):** A measure of the amount of oxygen dissolved in water.

**pH:** A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

**Reach:** A specific portion or segment of a stream.

**Sediment:** Soil and organic matter that is covered with water (for example, river or lake bottom).

**Streamflow (flow):** Discharge of water in a surface stream (river or creek).

**Total Maximum Daily Load (TMDL):** A distribution of a substance in a water body designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

**Total suspended solids (TSS):** Portion of solids retained by a filter.

**Watershed:** A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

**303(d) list:** Section 303(d) of the federal Clean Water Act, requiring Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

## Acronyms and Abbreviations

DOC	Dissolved organic carbon
Ecology	Washington State Department of Ecology
e.g.	For example
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
i.e.	In other words
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
PBDE	polybrominated diphenyl ethers
PCB	polychlorinated biphenyls
QA	Quality assurance
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
TMDL	(See Glossary above)
TOC	Total organic carbon
TSS	(See Glossary above)
USGS	United States Geological Survey
WRIA	Water Resource Inventory Area
WSTMP	Washington State Toxics Monitoring Program

### *Units of Measurement*

°C	degrees centigrade
cfs	cubic feet per second
dw	dry weight
ft	feet
L	liter
pg/L	picograms per liter (parts per quadrillion)
ug/Kg	micrograms per kilogram (parts per billion)
um	micrometer

## Quality Assurance Glossary

**Accreditation:** A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)...that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

**Accuracy:** The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms precision and bias be used to convey the information associated with the term accuracy. (USGS, 1998)

**Analyte:** An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella. (Kammin, 2010)

**Bias:** The difference between the population mean and the true value. Bias usually describes a systematic difference reproducible over time, and is characteristic of both the measurement system, and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI). (Kammin, 2010; Ecology, 2004)

**Blank:** A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process. (USGS, 1998)

**Calibration:** The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured. (Ecology, 2004)

**Check standard:** A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards, but should be referred to by their actual designator, e.g., CRM, LCS. (Kammin, 2010; Ecology, 2004)

**Comparability:** The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator. (USEPA, 1997)

**Completeness:** The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator. (USEPA, 1997)

**Continuing Calibration Verification Standard (CCV):** A QC sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run. (Kammin, 2010)



**Control chart:** A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system. (Kammin, 2010; Ecology 2004)

**Control limits:** Statistical warning and action limits calculated based on control charts. Warning limits are generally set at  $\pm 2$  standard deviations from the mean, action limits at  $\pm 3$  standard deviations from the mean. (Kammin, 2010)

**Data Integrity:** A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading. (Kammin, 2010)

**Data Quality Indicators (DQI):** Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity. (USEPA, 2006)

**Data Quality Objectives (DQO):** Qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions. (USEPA, 2006)

**Data set:** A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010)

**Data validation:** An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment, and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier, data is usable for intended purposes.
- J (or a J variant), data is estimated, may be usable, may be biased high or low.
- REJ, data is rejected, cannot be used for intended purposes (Kammin, 2010; Ecology, 2004).

**Data verification:** Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set. (Ecology, 2004)

**Detection limit** (limit of detection): The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero. (Ecology, 2004)

**Duplicate samples:** Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis. (USEPA, 1997)

**Field blank:** A blank used to obtain information on contamination introduced during sample collection, storage, and transport. (Ecology, 2004)

**Initial Calibration Verification Standard (ICV):** A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples. (Kammin, 2010)

**Laboratory Control Sample (LCS):** A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples. (USEPA, 1997)

**Matrix spike:** A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects. (Ecology, 2004)

**Measurement Quality Objectives (MQOs):** Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness. (USEPA, 2006)

**Measurement result:** A value obtained by performing the procedure described in a method. (Ecology, 2004)

**Method:** A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed. (EPA, 1997)

**Method blank:** A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples. (Ecology, 2004; Kammin, 2010)

**Method Detection Limit (MDL):** This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of

an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero. (Federal Register, October 26, 1984)

**Percent Relative Standard Deviation (%RSD):** A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\%RSD = (100 * s)/x$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010)

**Parameter:** A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all “parameters.” (Kammin, 2010; Ecology, 2004)

**Population:** The hypothetical set of all possible observations of the type being investigated. (Ecology, 2004)

**Precision:** The extent of random variability among replicate measurements of the same property; a data quality indicator. (USGS, 1998)

**Quality Assurance (QA):** A set of activities designed to establish and document the reliability and usability of measurement data. (Kammin, 2010)

**Quality Assurance Project Plan (QAPP):** A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives. (Kammin, 2010; Ecology, 2004)

**Quality Control (QC):** The routine application of measurement and statistical procedures to assess the accuracy of measurement data. (Ecology, 2004)

**Relative Percent Difference (RPD):** RPD is commonly used to evaluate precision. The following formula is used:

$$[\text{Abs}(a-b)/((a + b)/2)] * 100$$

where “Abs()” is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology, 2004).

**Replicate samples:** Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled. (USGS, 1998)

**Representativeness:** The degree to which a sample reflects the population from which it is taken; a data quality indicator. (USGS, 1998)

**Sample (field):** A portion of a population (environmental entity) that is measured and assumed to represent the entire population. (USGS, 1998)

**Sample (statistical):** A finite part or subset of a statistical population. (USEPA, 1997)

**Sensitivity:** In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit. (Ecology, 2004)

**Spiked blank:** A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method. (USEPA, 1997)

**Spiked sample:** A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency. (USEPA, 1997)

**Split Sample:** The term split sample denotes when a discrete sample is further subdivided into portions, usually duplicates. (Kammin, 2010)

**Standard Operating Procedure (SOP):** A document which describes in detail a reproducible and repeatable organized activity. (Kammin, 2010)

**Surrogate:** For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis. (Kammin, 2010)

**Systematic planning:** A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning. (USEPA, 2006)

## References for QA Glossary

Ecology, 2004. Guidance for the Preparation of Quality Assurance Project Plans for Environmental Studies. <http://www.ecy.wa.gov/biblio/0403030.html>

Kammin, B., 2010. Definition developed or extensively edited by William Kammin, 2010. Washington State Department of Ecology, Olympia, WA.

USEPA, 1997. Glossary of Quality Assurance Terms and Related Acronyms. U.S. Environmental Protection Agency. <http://www.ecy.wa.gov/programs/eap/quality.html>

USEPA, 2006. Guidance on Systematic Planning Using the Data Quality Objectives Process EPA QA/G-4. U.S. Environmental Protection Agency. <http://www.epa.gov/quality/qs-docs/g4-final.pdf>

USGS, 1998. Principles and Practices for Quality Assurance and Quality Control. Open-File Report 98-636. U.S. Geological Survey. <http://ma.water.usgs.gov/fhwa/products/ofr98-636.pdf>